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Imine Bridged Planar Poly(*p*-phenylene) Derivatives for Maximization of Extended p-Conjugation. The Common Intermediate Approach

by

Jaydeep J. S. Lamba and James M. Tour

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Department of Chemistry and Biochemistry
University of South Carolina
Columbia, SC 29208

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13. ABSTRACT

Described are two approaches to planar conjugated poly(*p*-phenylene) (PPP) derivatives. The first approach, involving lactam bridges, was unsuccessful due to the insolubility of the 6(5*H*)-phenanthridinonyl moieties. The second approach, which utilized imine bridges, worked excellently since the compounds were generally soluble and the bridge formations were highly efficient. The main PPP backbone was synthesized via Pd(0)-catalyzed coupling of an arylbis(boronic ester) with an aryldibromide. Imine bridges, that are formed by exposure of the polymer to trifluoroacetic acid or HCl, force the consecutive units into planarity. The bridging units are sp^2 hybridized thus allowing for greater π-electron flow between the consecutive phenyl units. The polymers, upon planarization, exhibit enormous bathochromic shifts of 210-240 nm. The optical spectra of the planar systems are compared to that of the parent nonplanarized polymers, oligo(*p*-phenylenes), PPP, and other near-planar PPP derivatives. When the bridges were *n*-dodecyl- or *n*-octylphenyl-substituted, the fully planar structures could be made into flexible free standing films. Additionally, an improved method is described in which a common intermediate, an aryl dibromodiacylhalide, could be used to prepare both the A and B units for the AB-type step growth polymerization. In one case, a selective alkylation or arylation of the acyl portions was accomplished using lower order cyanocuprates or Pd(0)-catalyzed ketone formation.

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Jaydeep J. S. Lamba and James M. Tour*

Department of Chemistry and Biochemistry

University of South Carolina

Columbia, South Carolina 29208

Abstract

Described are two approaches to planar conjugated poly(*p*-phenylene) (PPP) derivatives. The first approach, involving lactam bridges, was unsuccessful due to the insolubility of the 6(5*H*)-phenanthridinonyl moieties. The second approach, which utilized imine bridges, worked excellently since the compounds were generally soluble and the bridge formations were highly efficient. The main PPP backbone was synthesized via Pd(0)-catalyzed coupling of an arylbis(boronic ester) with an aryldibromide. Imine bridges, that are formed by exposure of the polymer to trifluoroacetic acid or HCl, force the consecutive units into planarity. The bridging units are sp^2 hybridized thus allowing for greater π-electron flow between the consecutive phenyl units. The polymers, upon planarization, exhibit enormous bathochromic shifts of 210-240 nm. The optical spectra of the planar systems are compared to that of the parent nonplanarized polymers, oligo(*p*-phenylenes), PPP, and other near-planar PPP derivatives. When the bridges were *n*-dodecyl- or *n*-octylphenyl-substituted, the fully planar structures could be made into flexible free standing films. Additionally, an improved method is described in which a common intermediate, an aryl dibromodiacylhalide, could be used to prepare both the A and B units for the AB-type step growth polymerization. In one case, a selective alkylation or arylation of the acyl portions was accomplished using lower order cyanocuprates or Pd(0)-catalyzed ketone formation. For the second monomer, a bis-Curtius rearrangement, in the presence of *tert*-butanol, converted both carbonyl moieties to BOC protected amines.

Poly(*p*-phenylene) (PPP),[1] a highly insoluble polymer that has been studied extensively for its possible electronic and photonic applications, has a 23° twist[1c,2] between the consecutive aryl units due to ortho hydrogen interactions (Fig 1). Attempts to enhance the solubility by

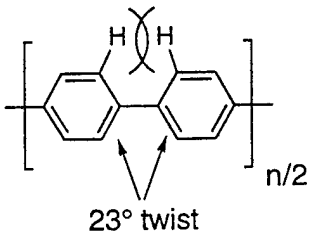


Figure 1. Structure of PPP, with a 23° twist between the consecutive aryl units due to ortho hydrogen interactions.

substitution of the rings forces the consecutive aryl units even further out of plane resulting in a plummet of the extended conjugation (easily observed by the optical spectra).[1]

Recently, there has been a large amount of synthetic activity to prepare and exploit such planarized PPP systems.[3] Müllen *et al.*, Scherf *et al.*, and Swager *et al.* have prepared all-carbon frameworks to induce covalent planarization in soluble ladder PPP derivatives.[4] We recently described the preparation of imine-bridged PPP.[5] Here we describe the full details of our approaches to ladder PPP derivatives with bridges that (1) form in high yields upon protonic activation once the PPP backbone is intact, (2) can be substituted so that the newly formed polymers are soluble, unlike many other aromatic ladder polymers, (3) contain a double-bonded unit to keep the consecutive aryl units planar while maximizing extended π-conjugation through the PPP backbone thereby increasing the band width (lowering the band gap) (Fig 2),[1c] and (4)

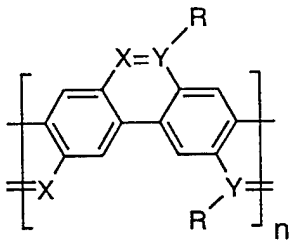
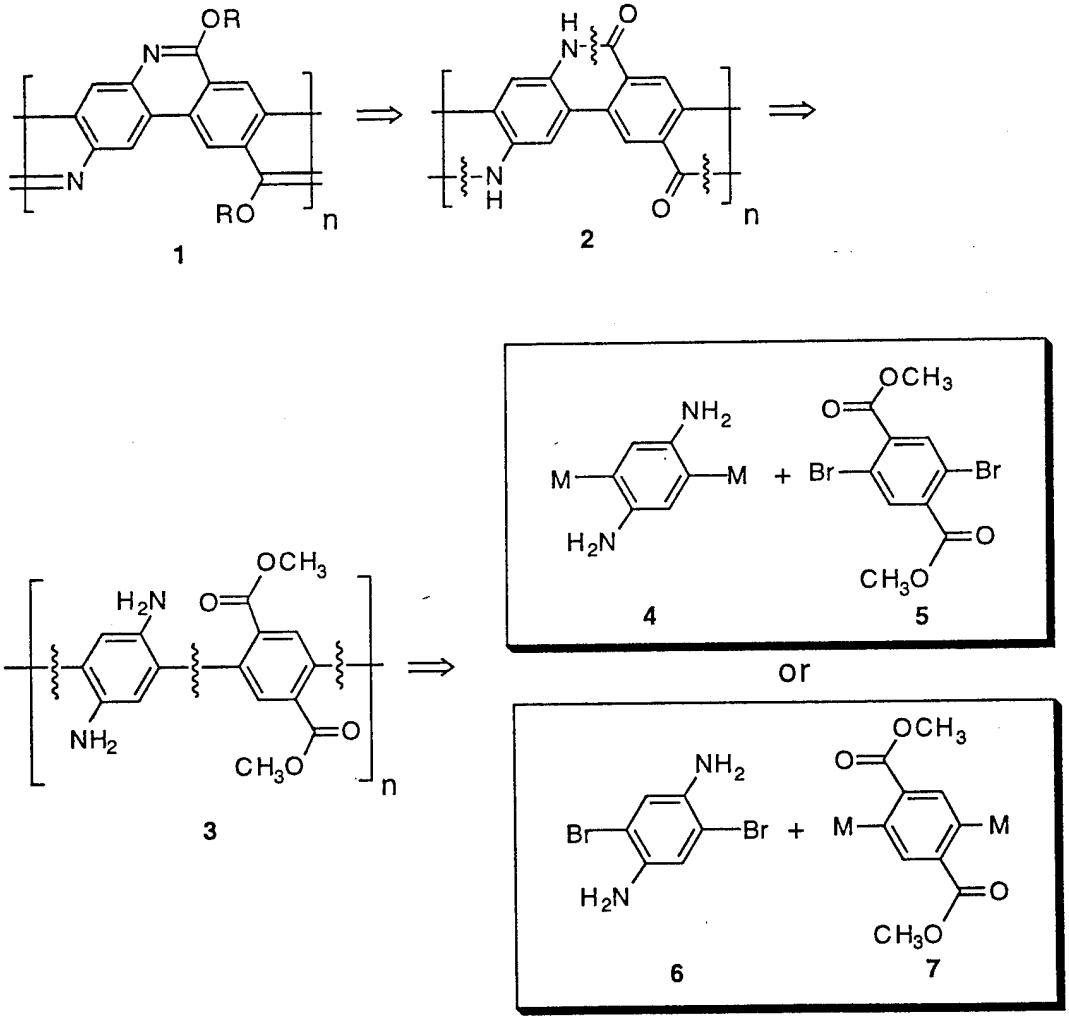


Figure 2. The consecutive benzenoid rings are help planar by the double-bonded bridging units so as to maximize the extended π-conjugation. The R groups permit solubility of the planar system.

can be solution-cast in the uncyclized form followed by protonic activation to obtain flexible free-standing films of the planarized system. We also describe here, for the first time, a new synthetic approach to both the A and B components of the polymer from a common monomeric intermediate.

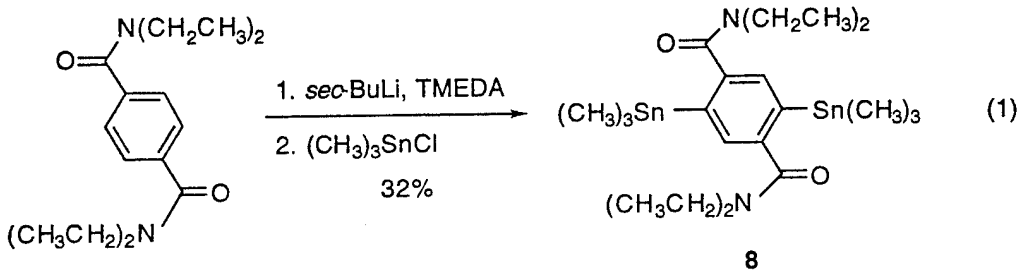
Our original retrosynthetic approach to planar PPP derivatives is outlined in Scheme 1.

Scheme I



We proposed the formation of the planar **1** to be prepared from O-alkylation of the lactam-bridged PPP **2** which contained 6(5*H*)-phenanthridinonyl moieties. In turn, **2** was to be prepared by lactamization of **3** which could be obtained from the dimetallated diamine **4** and the dibrominated diester **5**, or their complements **6** and **7**.

In an attempt to explore the efficacy of the retrosynthetic route detailed in Scheme I, the dimetallated diamide **8** (eq 1) was prepared by a bis(*ortho*-lithiation) and stannylation.[6]



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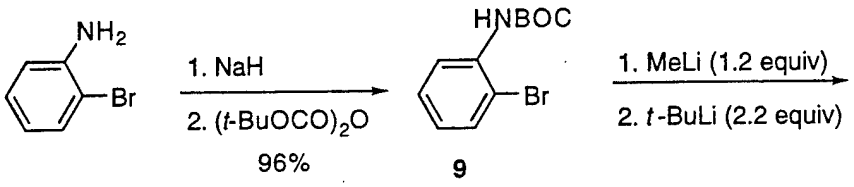
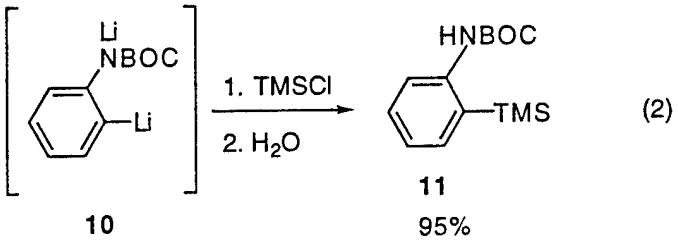
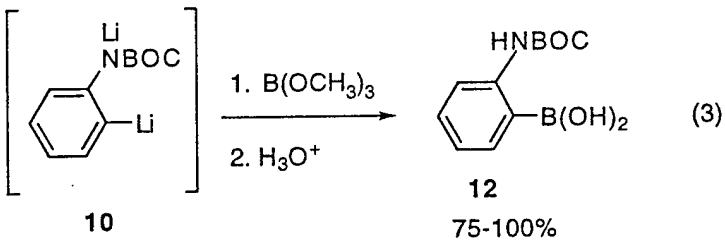
However, Pd(0)-catalyzed coupling of **8** with 2-iodoaniline, *N*-(acetyl)-2-iodoaniline, or even iodobenzene, gave very low yields of the cross coupled products. In light of these initial results and the fact that Pd(0)-catalyzed oxidative addition reactions are facilitated with electron deficient ring systems,[7] we chose to keep the halides on the aromatic carbonyl portion and the metals on the aminated monomer, namely **4** plus **5** (Scheme I). Additionally, reported Pd(0)-catalyzed cross coupling yields of arylboronic acids[7] are superior to yields reported for arylstannanes,[8] therefore, most further attempts were conducted with the boronic acids and boronic acid derivatives.

In order to prepare the material necessary for further model studies, we attempted to directly *ortho*-lithiate *N*-(*tert*-butoxycarbonyl)aniline with alkyllithium reagents followed by quenching with TMSCl to check the efficiency of the BOC directed *ortho*-lithiations.[9] However, the reactions were repeatedly low-yielding. Therefore, we turned our attention to lithium-halogen exchange reactions. BOC protection of 2-bromoaniline with THF/NaOH afforded only 21% yield of **9** while NaH-promoted protection was high-yielding (eq 2). Abstraction of the

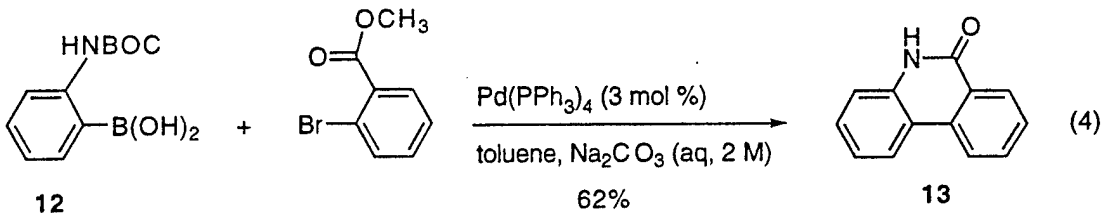




N-H proton with MeLi followed by lithium-halogen exchange with *tert*-BuLi afforded a nearly quantitative yield of the dilithio-intermediate **10**, confirmed by quenching with TMSCl and isolation of **11** after aqueous workup (eq 2). Note that simply an excess of *tert*-BuLi, without MeLi treatment, is problematic because lithium-halogen exchange with *tert*-BuLi (but not MeLi) is faster than deprotonation of the BOC-protected amine, resulting in proton transfer and overall reduction of **9**.[10] Thus the successive addition of the two different alkyllithium reagents is required. Following an analogous protocol, **10** was quenched with trimethylborate and hydrolyzed to afford the boronic acid **12** (eq 3). **12** was contaminated with some boron salts, but



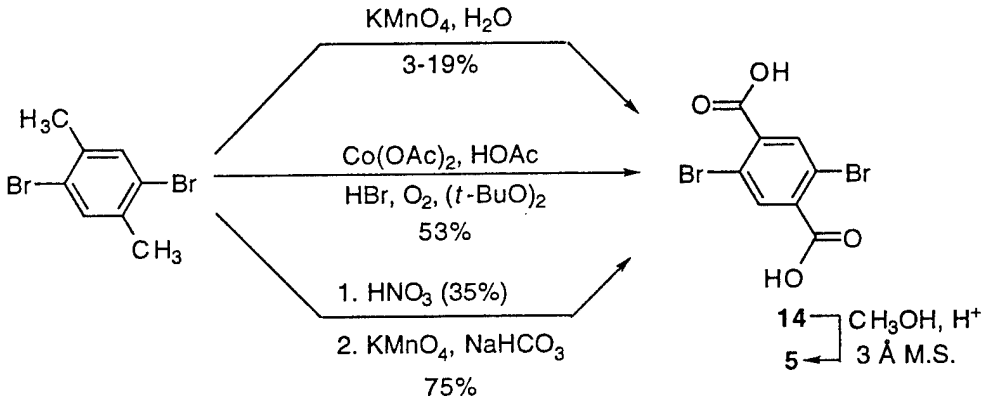
before perfecting the purification methods, we investigated the coupling process. Treatment of **12** with 2-bromomethylbenzoate and Pd(0) afforded the desired dimer which, under the reaction conditions, concomitantly lactamized (eq 4). Certainly, the coupling yield would have to be



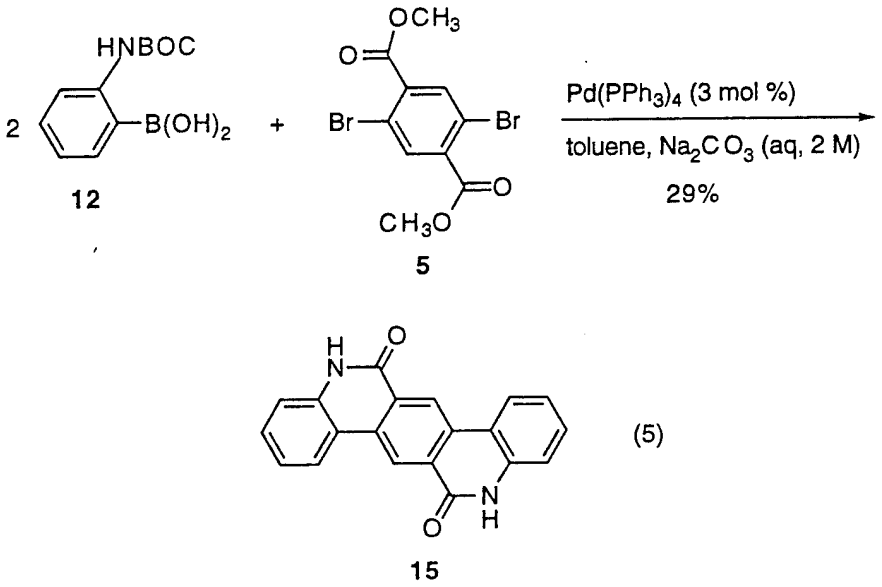
improved before we could proceed with a polymerization reaction, but the results were encouraging and further model studies were in order.

We then proceeded to prepare the dibromodiester **5**. Aqueous $KMnO_4$ oxidation of 2,5-dibromo-1,4-dimethylbenzene afforded low yields of the diacid **14**. The cobalt-based oxidation was superior, after purifying as the dimethylester **5**,[11] but we finally opted for a two-step oxidation process which gave the highest yields of the diacid **14**.[12] Fischer esterification afforded **5** (Scheme II).

Scheme II



Pd(0)-catalyzed cross coupling of **12** with **5** to form the trimer **15** was then carried out (eq 5). Lactamization occurred, and again, the coupling conditions were not optimized.

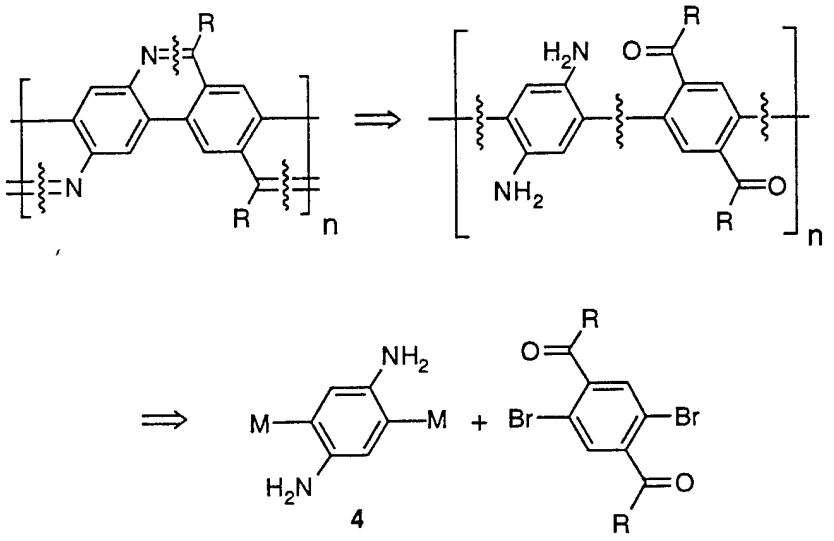


(5)

Unfortunately, we discovered that this methodology was flawed in that **15** was nearly insoluble even in $CHCl_3$. In fact, **15** was isolated by heating the crude reaction mixture in $CHCl_3$, and filtering off the insoluble **15** which could be characterized only by FTIR and mass spectrometry due to its insolubility. Since even the trimer **15** was insoluble, utilization of this approach for the formation of the polymer would be unsuitable.

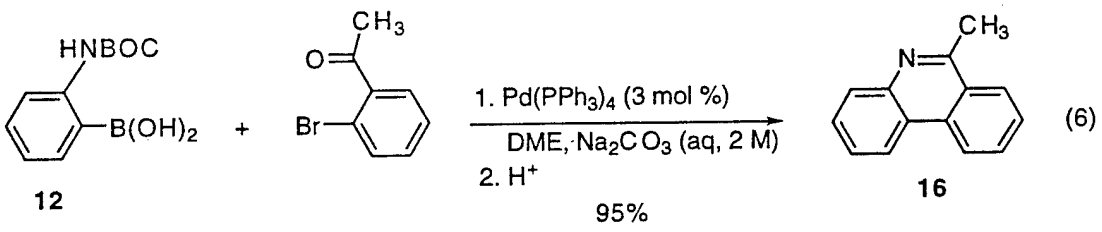
We then modified our approach to avoid the formation of lactams due to their poor solubility characteristics. We also sought to have the solubilizing units intact during the cross coupling and prior to the planarization. Our second retrosynthetic approach is outlined in Scheme III. Here we rely on a high-yielding imine formation to induce the planarization

Scheme III



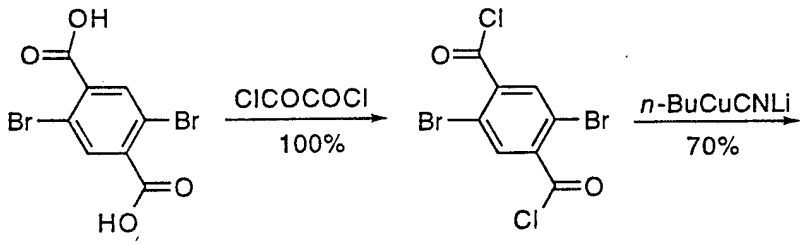
rather than lactam moieties.

To explore this new synthetic approach, we treated **12** with 2-bromoacetophenone under the Gronowitz modified Suzuki cross coupling conditions.[7c] The coupling conditions worked superbly to afford, after acid-catalyzed BOC removal and imine formation, the dimer **16** (eq 6).

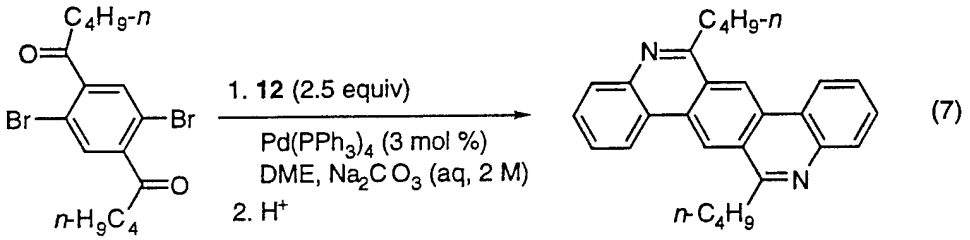


When we used the trimethylstannyl derivative of **12** rather than the boronic acid, the yield of **16** was reduced to <30%, while under modified Stille coupling conditions, the yields were 46-65%.[8,13] This confirmed our original findings that Stille couplings were inferior for this aryl-aryl cross coupling. We also attempted to prepare the 9-BBN derivative of **12** rather than the boronic acid, however, air decomposition was occurring.[14] Thus the boronic acids were superior.

We then proceeded to prepare the dibromodiketone **18** from **14** by using a lower order cyanocuprate addition to the diacid chloride **17** followed by Pd(0)-coupling with **12** to afford the trimer **19** in excellent yield (eq 7). Moreover, **19** was quite soluble in numerous organic



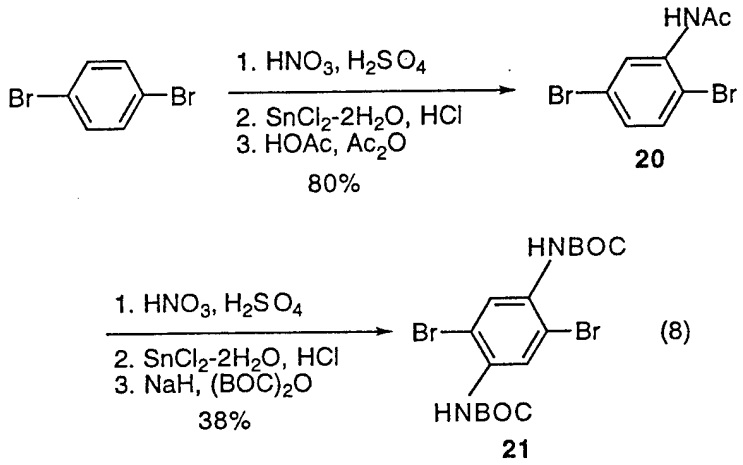
14 17



18 19 (7)

solvents. Thus this appeared to be an excellent approach to the planar PPP derivatives.

With the methodological findings now backing us, the most challenging synthetic part of our studied remained, namely, the preparation of the dimetallated diamine **4**. Based on our synthesis of **12**, we proceeded to prepare a dibrominated diamine **21** (eq 8).[15] This procedure

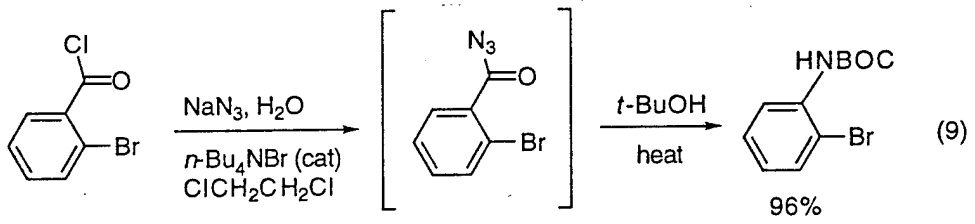


20 **21** (8)

worked acceptably on several occasions. However, *CAUTION*, on one occasion, after the nitration of **20**, the material exploded violently while vacuum drying in a desiccator. We presumed that it was due to the formation of small amounts of the dinitroaromatic amine. After subsequent nitrations of **20**, we never attempted to dry the material; we would simple reduce the wet filtered compound with $SnCl_2$. *CAUTION*, on a second occasion after completion of the nitration of **20**,

the flask was opened to air and the mixture began to rapidly exotherm and smoke profusely before it was quenched with ice water, preventing what may have been another violent explosion. An alternate route to the preparation of **21** was therefore sought, preferably one that would permit the use of the common intermediate **17** via a Curtius rearrangement. This could significantly enhance the efficiency of the synthesis.

In exploring the possibility of using a Curtius rearrangement approach, 2-bromobenzoyl chloride was transformed to the acyl azide under phase transfer conditions[16] using 1,2-dichloroethane as a cosolvent. We avoided the use of dichloromethane since sodium azide/dichloromethane mixtures have been reported to occasionally detonate.[17] Once the acyl azide was formed, the mixture was heated to affect the Curtius rearrangement. When we carried out the rearrangement in the presence of *tert*-butanol, the BOC protected product was afforded in excellent yield (eq 9).[16e] Extension of this to the formation of **21** proceeded well, though the



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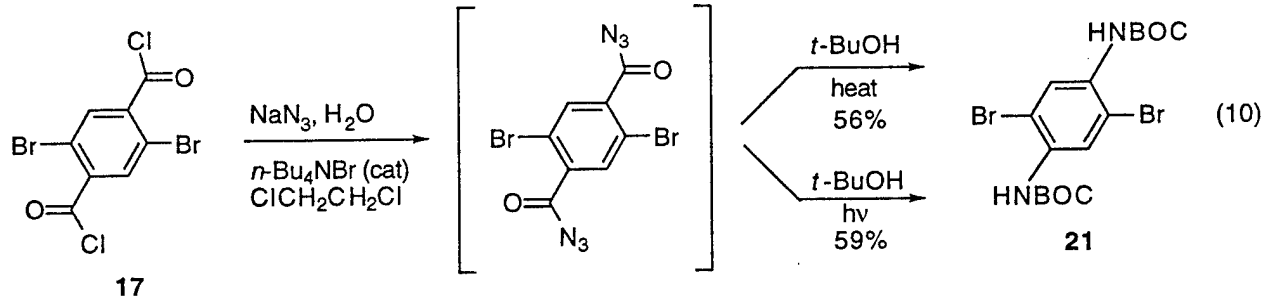
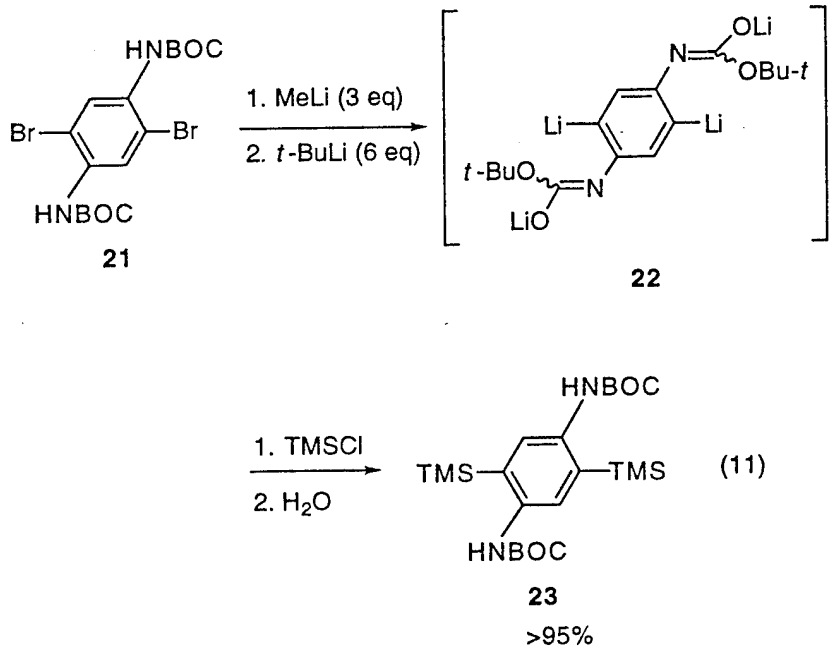
yields were somewhat lower than in the monoacyl azide case (eq 10). We attribute this to the



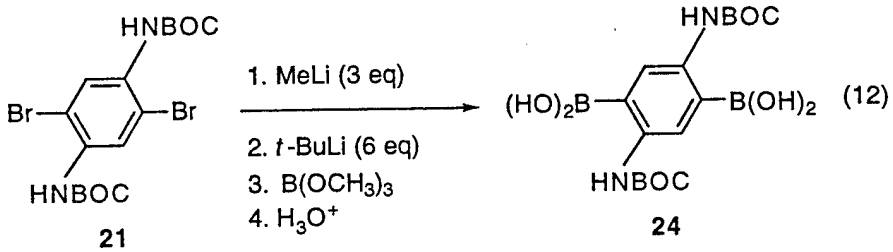
(10)

low solubility of the bisacyl azide. The yield of **21** was nearly identical whether the rearrangement was carried out thermally or photochemically. Thus the common intermediate, **17**, could be used to prepare both the A and B components of the AB-type step growth polymerization reaction.

Remaining was the dimetallation of **21** via bis-lithium-halogen exchange in a manner similar to that used in eq 3 for the preparation of **12**. As a check for the lithiation efficiency, **21**, which is nearly insoluble in ether, was suspended in ether at 23 °C, and MeLi was slowly added while methane evolution was observed. The dilithio compound was then cooled and *tert*-BuLi was added to affect the lithium-halogen exchange. The mixture was allowed to warm to 0 °C and the now soluble tetralithio intermediate **22** was quenched with TMSCl and then water to afford >95% yield of **23** (eq 11). Therefore, the tetralithiation worked remarkably well and we

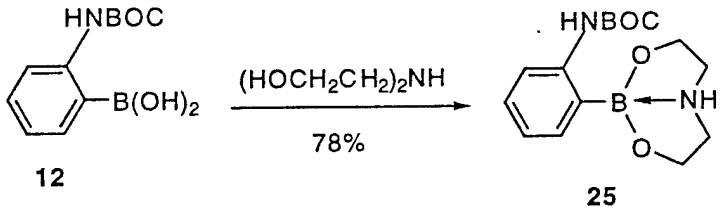


proceeded to prepare the bis(boronic acid) **24** (eq 12). Unfortunately, we had much difficulty

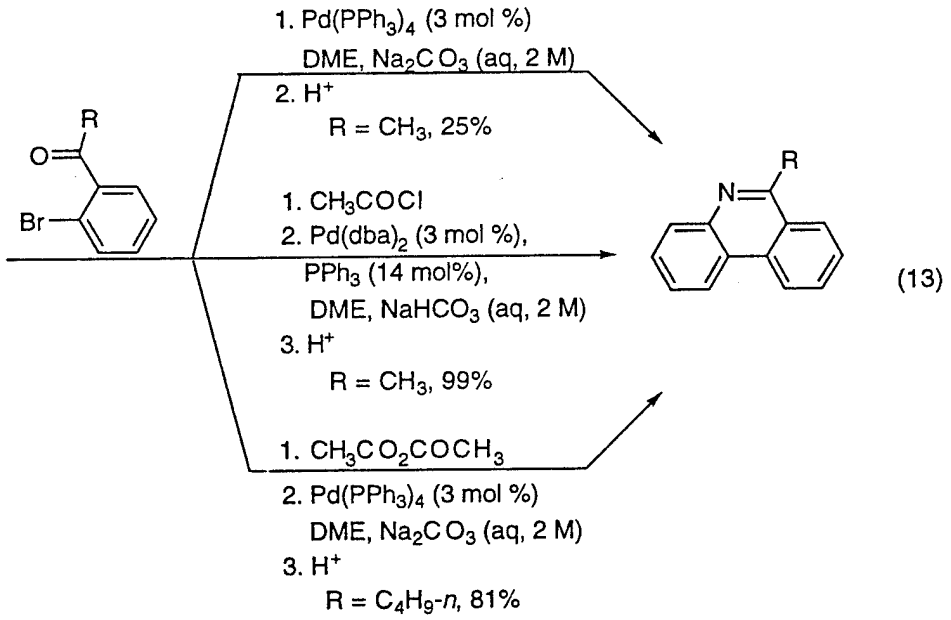


isolating **24** due to decomposition and/or extraction difficulties from the aqueous phase. Thus it could never be adequately purified for the step growth polymerization; a process requiring highly pure starting materials.

We then sought to use boronic acid derivatives which could facilitate the purification but could be equally efficient in the cross coupling process. Though diethanolamine complexes of boron are reported to usually be crystalline solids, their efficiency in cross coupling reactions is minimal.[18] We investigated this by preparing the crystalline solid **25**, and subjecting it to the cross coupling conditions (eq 13). As reported, the diethanolamine-boron complexes do not



12 **25**

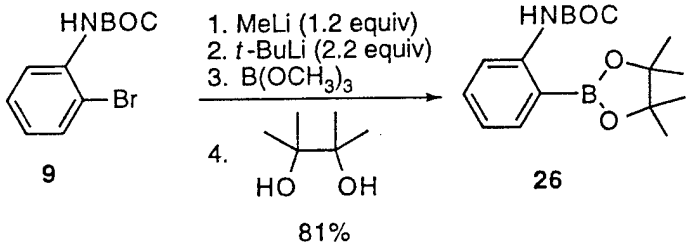


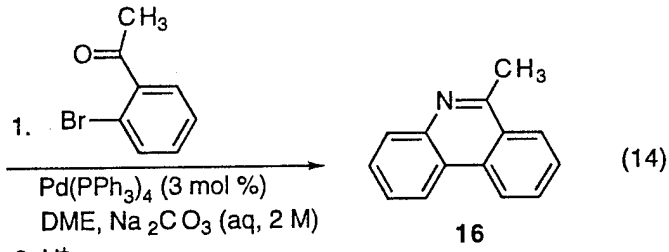
(13)

participate well under standard cross coupling conditions; the yield was only 25%. However, we were able to develop methods to significantly increase the yields in the cross couplings involving this boron complex. We first deactivated the nitrogen donation into the boron atom by,

presumably, acylation of the amine, then subjecting the mixture to the cross coupling conditions. The yield of the cross coupling reactions increased to 81-99% (eq 13). We present this cross coupling modification here since it could be suitable for many transformations, and we have further developments in progress. Unfortunately, we discovered this acylation protocol late in our planar PPP research, and studies using the pinacol borate esters were already well underway in this laboratory.

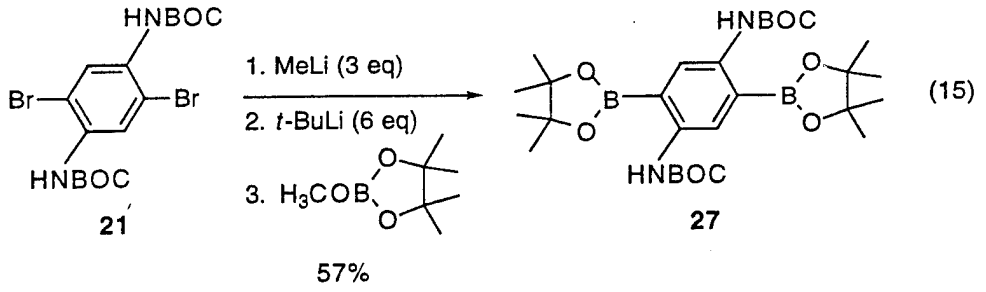
Others have used glycol[1h] and 1,3-propane diol[4g,h] borate esters for polymer synthesis, but we found these to be too labile for the chromatographic purifications needed in our systems. Note that our compounds may be unique in that there could exist BOC-carbonyl electron donation into the empty p-orbital of the boron atoms. We then prepared the pinacol borate ester **26**, by pinacol exchange with the dimethylborate ester, which could be purified by chromatography on triethylamine-deactivated silica gel. **26** cross coupled superbly to afford a very high yield of **16** (eq 14).





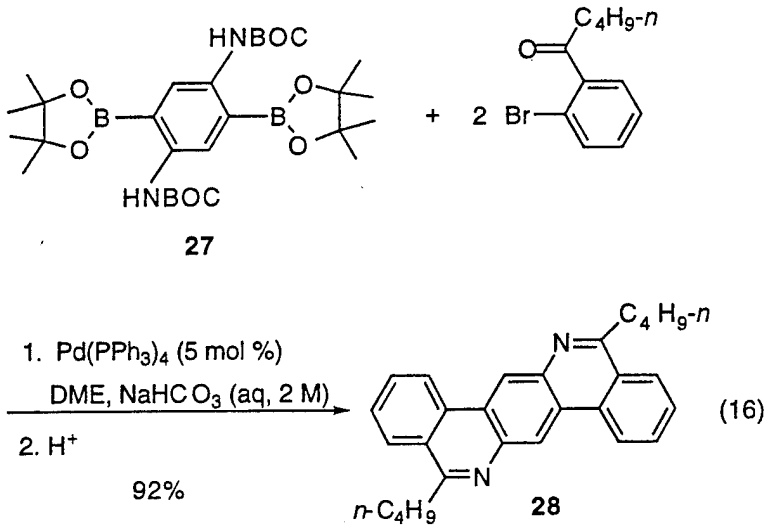
(14)

Remaining was the preparation of the bisboronic ester from the dilithio intermediate **22**. Though it proved to be a difficult and time consuming task to generate material that was of sufficient purity (>99.9%) for the cross coupling reaction, ultimately, the adequate synthesis and purification conditions for **27** were discovered (eq 15). Tetralithiation of **21** and quenching with



methyl pinacol borate afforded the monomer **27** which could be purified by passage through a flash chromatography column containing a mixture of activated charcoal and Celite as the stationary phase and CH_2Cl_2 as the eluant, followed by recrystallization to form pure **27** in 57% yield. Alternatively, we could use neutral alumina for the chromatography using 1:1 CH_2Cl_2/EtOAc to rapidly move **27** through the column prior to significant decomposition. Silica gel or even amine-washed silica gel caused rapid decomposition of **27**. We later found that the formation of troublesome borate salts could be retarded if, after the addition of methyl pinacol borate, excess pinacol was added followed by a fast wash with dilute HCl (aq).

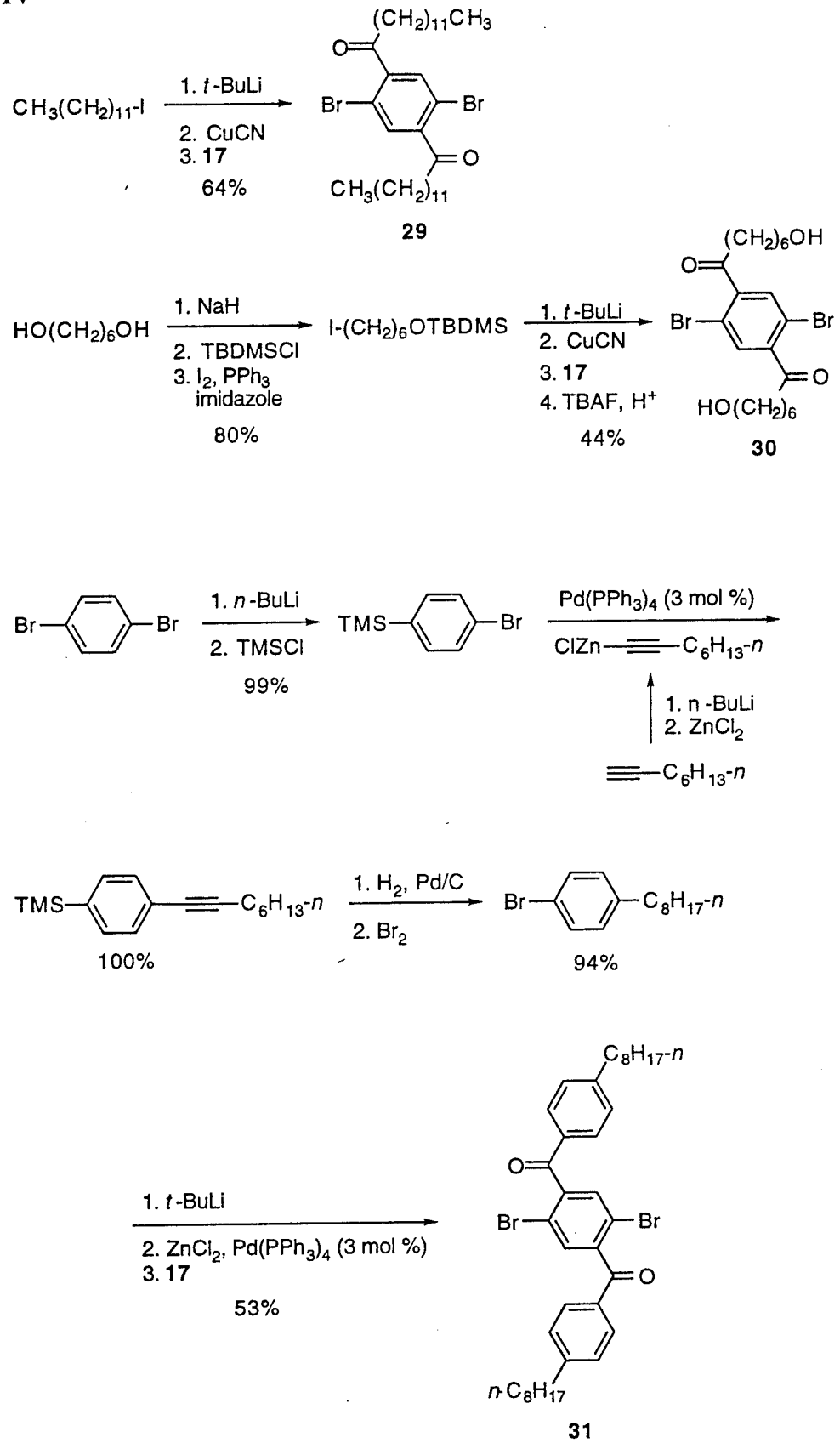
Optimization studies on the cross coupling reaction were carried between **27** and each of the following three aryl bromides: bromobenzene, 2-bromoacetophenone, and 2-bromophenyl butyl ketone (prepared from 2-bromobenzoyl chloride and *n*-BuCuCNLi). We screened numerous non-aqueous[14] (DMF, DME, dioxane, DMPU, plus TMSONa, K_3PO_4-H_2O, or K_2CO_3 with and without *n*-Bu_4NBr) and aqueous conditions[7,14,18] (DME/H_2O, DMF/H_2O, $PhNO_2$/H_2O, plus K_2CO_3, Cs_2CO_3, Na_2CO_3, Tl_2CO_3, or $NaHCO_3$). The aqueous conditions afforded higher yields and the affect of the base upon the yield of the cross coupling reaction appeared to be most important. Highest yields were obtained with milder bases, and sodium bicarbonate proved to work the best for the formation of the trimer **28** (eq 16). Note that the



yield of 92% for **28** was using a non-crystalline sample of **27**. We later learned (see below), during the polymerization optimization studies, that use of highly pure crystalline **27** was important for very efficient coupling to occur. Hence, the 92% isolated yield of **28** is not representative of the high efficiency that can be attained in this cross coupling reaction since the optimal cross coupling conditions were subsequently determined.

Before describing the details of the polymerization, Scheme IV outlines the preparation of three dibromodiketone monomers, **29-31**, that were used in addition to **18**.

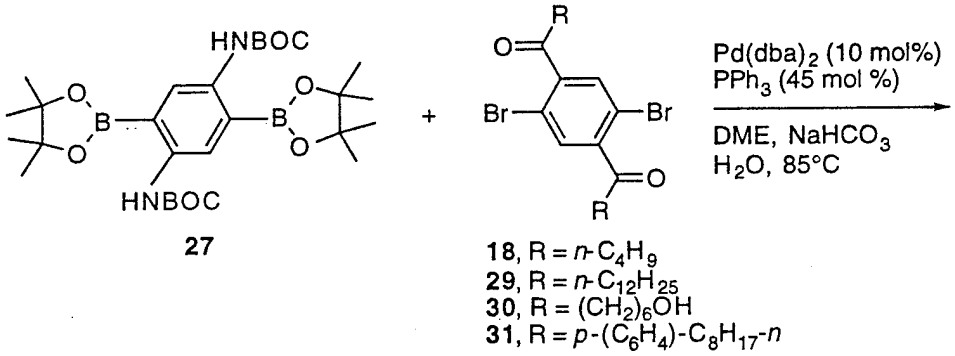
Scheme IV

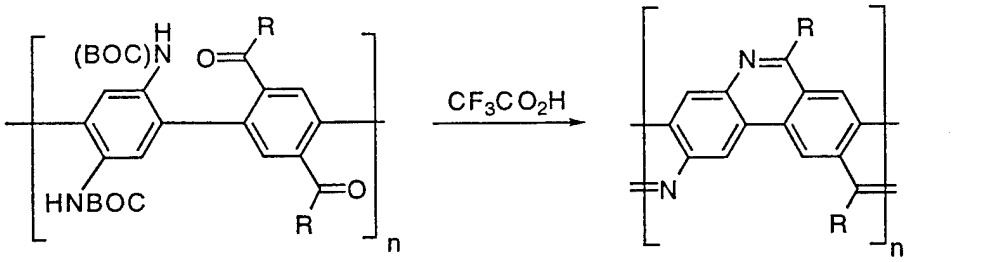

CH3(CH2)11-I
1. t-BuLi
2. CuCN
3. 17
64%
(CH2)11CH3
O
Br
Br
O
CH3(CH2)11
29
HO(CH2)6OH
1. NaH
2. TBDMSCl
3. I2, PPh3
imidazole
80%
I-(CH2)6OTBDMS
1. t-BuLi
2. CuCN
3. 17
4. TBAF, H+
44%
(CH2)6OH
HO(CH2)6
30
Pd(PPh3)4 (3 mol %)
ClZn—≡—C6H13-n
1. n-BuLi
2. ZnCl2
≡—C6H13-n
TMS
C6H13-n
100%
1. H2, Pd/C
2. Br2
C8H17-n
94%
1. t-BuLi
2. ZnCl2, Pd(PPh3)4 (3 mol %)
3. 17
53%
n-C8H17
31

Lithiation of iododododecane, transmetallation to the lower order cyanocuprate, and addition to **17** afforded the bis(dodecyl)ketone **29**. Monosilylation of 1,6-hexanediol,[19] iodination,[20] lithiation, addition to **17** via the cyanocuprate, and desilylation afforded **30**. Desilylation with non-acidic TBAF appeared to cause fluoride conjugate addition with bromide displacement. Monolithiation of 1,4-dibromobenzene, silylation, and cross coupling with the alkynyl zinc reagent afforded 1-octynyl-4-trimethylsilylbenzene. Reduction, bromodesilylation, conversion of the bromide to the chlorozinc arene, and cross coupling with **17** provided **31**. At this point, we had several complementary dibromodiketone monomers for the final polymerization process.

The polymerizations of **27** with **18**, and **29-31** were then conducted (Scheme V).

Scheme V





32, R = *n*-C_4H_9, 63%,
M_n = 9,850, M_w/M_n = 1.85
33, R = *n*-$C_{12}H_{25}$, 97%,
M_n = 28,400, M_w/M_n = 3.70
34, R = $(CH_2)_6OH$, 82%,
insoluble
35, R = *p*-(C_6H_4)-C_8H_{17}-*n*, 80%
M_n = 18,500, M_w/M_n = 2.75

36, R = *n*-C_4H_9, 90%
37, R = *n*-$C_{12}H_{25}$, 97%,
38, R = *p*-(C_6H_4)-C_8H_{17}-*n*, 99%

Highest molecular weights were obtained with (1) $Pd(PPh_3)_4$ generated in situ from $Pd(dba)_2$ and PPh_3, (2) the couplings carried out for ~24 h using an equimolar mixture of **27** to the diketone, followed by the addition of a 5-10 mol % excess of **27** with continued heating for 1-2 d, and (3) the use of **27** as large cubic crystals of extremely high purity; the use of needle-like crystals of **27** afforded polymers with substantially lower molecular weights. The yields listed were recorded by size exclusion chromatography (SEC) relative to polystyrene standards. Since size exclusion chromatography (SEC) is a measure of the hydrodynamic volume and not the molecular weight (MW), significant errors in M_n and M_w may result when comparing rigid rod polymers to the flexible coils of PS standards. Therefore, the values recorded here are given simply as a reference. While **32**, **33**, and **35** were soluble, **34** was insoluble, possibly due to enhanced crystallinity induced by hydrogen bonding with the hydroxyl moieties. Attempts to silylate the free hydroxyl groups after the polymerization were unsuccessful. Use of the silylated version of **30** for the initial polymerization was not attempted since, under the extended hot alkaline polymerization conditions, desilylation would most likely occur. Use of a more robust hydroxyl protecting group was not investigated.

As expected, upon exposure of **32**, **33**, or **35** to trifluoroacetic acid (TFA), quantitative loss of the BOC protecting group and cyclization afforded **36**, **37**, and **38**, respectively (Scheme V). Note that the twist angle in these planar PPP derivatives is <1° between the consecutive phenyl rings as calculated by MMX with extended π-Hückel parameters. As a testimony of the efficiency of this cyclization protocol, all stretches for the ketone, carbamate, and amine in **32**, **33**, and **35** were absent in the FTIR spectrum of **36-38**. While the elemental analysis data for **32**, **33**, and **35** agreed well with the calculated values, **36-38** had lower than calculated values for the carbon and hydrogen content. Since the nitrogen content generally agreed well with the theoretical values, and no TFA was noticed in FTIR spectra of the base-washed cyclized polymers, there might have been difficulty in complete combustion of these highly unsaturated compounds.

Samples of **36-38** can be solubilized with CH_2Cl_2/TFA (2:3) mixtures. Additionally, **33** can form THF solution-cast films then be cleanly cyclized by suspension of the

film in anhydrous HCl/EtOAc followed by proton removal with Et_3N/NaOH to afford **37** as a flexible free-standing film. Again, this film was devoid of ketone, carbamate, and amine absorptions in the FTIR spectrum. Therefore, the dodecyl groups are apparently exerting a plasticizing effect so that even this planar rigid rod polymer can possess good film-forming properties. A film of **38** was similarly prepared though it was somewhat more brittle than the film of **37**.

Powder X-ray diffraction (XRD) of annealed **36** showed a broad pattern at 14 and 41 Å while **37** showed a similar pattern at 27 and 45 Å. Differential scanning calorimetry (DSC) (50-350°C, 20°C/min, N_2) thermograms of **36** and **37** were featureless on both the first and second heating cycles. Thermogravimetric analysis (TGA) (50-900°C, 20°C/min, N_2) of **37** showed an onset of major weight loss at 400°C, 10% weight loss at 434°C, and 50% weight loss at 550°C. The TGA thermogram of **36** was similar.

The conductivity studies on the planarized materials were discouraging. Undoped pressed pellets or films of **37** were insulating. P-dopants such as I_2 and $SbCl_5$ gave irreproducible conductivities of approximately 4-5 x 10^{-6} $\Omega^{-1}cm^{-1}$ (4-point probe). We had the notion that the imine moieties were making the polymer more electron deficient than most polyphenylenes and far more electron deficient than 5-membered heterocyclic polymers like polypyrrole or polythiophene. Thus, we attempted n-doping the films of **37** with sodium naphthalide; however, the doped films were too brittle for 4-point probe analysis.

Most exciting is the optical absorption data showing enormous bathochromic shifts in the polymers upon cyclization (conversion of **32** to **36**, **33** to **37**, and **35** to **38**) (Figure 3); an observation consistent with the proposed ladder formation (Table I). Also interesting are the large hypsochromic shifts in the spectrum of protonated **37** or **38** (solution in CH_2Cl_2/TFA, 2:3) relative to **37** or **38**, respectively, in the neutral form (solid), suggesting that cationic nitrogen atoms retard the extended conjugation. We also compared the polymer absorptions to those of the trimers **19** and **28**. The absorptions of these planar polymers are far more bathochromically-shifted than those of the planar trimers, oligo(*p*-phenylenes), and PPP,[21] while the λ_{max} values

are in the range of, or somewhat higher than those of the all carbon near-planar PPP derivatives that have been synthesized.[4] Thus the affect of the planarization on the extended π-conjugation is most evident.

In summary, we have described two approaches to planar conjugated PPP derivatives. The first approach, involving lactam bridges, was unsuccessful due to insolubility of the 6(5*H*)-phenanthridinonyl moieties. The second approach worked excellently since the compounds were generally soluble and the bridge formations were highly efficient. Additionally, described was a method in which a common intermediate, an aryl dibromodiacylhalide, could be used to prepare both the A and B units for the step-growth polymerization. In one case, a selective alkylation or arylation of the acyl portions was accomplished using lower order cyanocuprates or Pd(0)-catalyzed ketone formation. For the second monomer, a bis-Curtius rearrangement, in the presence of *tert*-butanol, converted both carbonyl moieties to BOC protected amines. And finally, the imine bridged planar PPP derivatives were far more bathochromically shifted than the non-planar PPPs, indicating greatly enhanced degrees of extended conjugation.

Acknowledgments. We are grateful for support from the Office of Naval Research and the National Science Foundation (EHR-91-08772, DMR-9158315), and generous industrial contributors to the NSF Presidential Young Investigator Award (1991-96): Hercules, IBM, Ethyl, Shell, Eli Lilly, Polaroid, Exxon, Molecular Design Ltd., and Farchan Corporations. David M. Lynn provided some technical assistance.

Supplementary Material Available: UV-visible spectra of compounds **32**, **33**, and **35-38**, in solution and as the film or solid powder. This material is contained in many libraries on microfiche, immediately following this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Experimental

General Procedures. All operations were carried out under a dry, oxygen-free, nitrogen atmosphere. Proton NMR spectra were recorded at 300 or 500 MHz on Brüker AM-300 or Brüker AM-500 spectrometers, respectively. The ^{13}C NMR spectra 75, or 125 MHz were recorded on Brüker AM-300 or Brüker AM-500 spectrometers, respectively. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS) and ^{13}C resonances were recorded using the 77.0-ppm $CDCl_3$ resonance of the solvent as an internal reference and are reported in ppm down field from TMS. Infrared (FTIR) spectra were recorded on a Perkin Elmer 1600 Series FTIR. The accurate-mass spectra were determined on a VG Analytical, Ltd., 70SQ high resolution, double-focusing mass spectrometer equipped with a VG 11/250 data system. Fast atom bombardment (FAB) mass spectra were recorded on the same instrument noted above and the isotopic ion distributions were compared with those calculated by the ISO program of VG Analytical, Ltd. Combustion analyses were obtained from Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091. Capillary GC analyses were obtained using a Hewlett Packard Model 5890 gas chromatograph using a Hewlett Packard 3396A integrator. Reagent grade diethyl ether, tetrahydrofuran (THF), and 1,4-dioxane were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade dichloromethane and toluene were distilled under nitrogen from CaH_2. Bulk grade hexane was distilled prior to use. Gravity column chromatography and flash chromatography was carried out on silica gel (230-400 mesh from EM Science).

2,5-Bis(trimethylstanyl)-1,4-bis-*N*,*N*-diethylbenzamide (8). The procedure was analogous to Snieckus *ortho*-lithiation methodology.[6] *sec*-Butyllithium (10.4 mL, 13.5 mmol, 1.3 M in cyclohexane) was added dropwise at -78° C to a solution of 1,4-bis-*N*,*N*-diethylbenzylamide (1.66 g, 6.0 mmol) in THF (36 mL) and TMEDA (1.57 g, 13.5 mmol). The solution was stirred for 1.5 h at -78°C and then trimethyltin chloride (2.73 g, 13.7 mmol) in THF (5 mL) was added. The solution was warmed to room temperature and stirred for 1.5 h. The reaction mixture was poured into water and then the organic layer was separated and extracted with ether (3x). The combined organic layers were washed with brine and dried over sodium sulfate.

The solvent was removed *in vacuo* to give the crude material which was purified by flash chromatography (silica gel, 4:1 hexanes: ether) which afforded 1.17g (32%) of the title compound as a white solid. FTIR (KBr) 2976, 2936, 1621, 1481, 1426, 1267, 1112, 1066, 864 777, 528 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 (s, 2 H), 3.55 (br s, 4 H), 3.25 (br s, 4 H), 1.25 (br s, 6 H), 1.06 (br s, 6 H), 0.24 (s, 18 H).

2-Bromo-*N*-(*t*-butoxycarbonyl)aniline (9). To a solution of sodium hydride (0.660 g, 27.5 mmol, 80% dispersion in mineral oil) in THF (150 mL) was added 2-bromoaniline (4.30 g, 2.73 mL, 25 mmol). The mixture was heated to reflux for 1 h, and then cooled to room temperature. Di-*tert*-butyldicarbonate (6.55 g, 6.9 mL, 30 mmol) was added and the slurry was stirred for 0.5 h. To the mixture, a second portion of sodium hydride (0.660 g, 27.5 mmol, 80% dispersion in mineral oil) was added and reaction was brought back to reflux for 14 h. The reaction was cooled to room temperature and carefully quenched with water. This mixture was extracted with ether (3x). The combined organic layers were washed with saturated ammonium chloride solution and saturated sodium bicarbonate solution and after drying over sodium sulfate, the solvent was removed *in vacuo* and the crude material was purified by flash chromatography [silica gel, hexanes/ether (20:1)] to afford 6.6 g (96%) of the title compound as an oil. FTIR (neat) 3416, 3072, 2979, 2931, 1736, 1592, 1519, 1434, 1368, 1247, 1223, 1157, 749 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 9.7 Hz, 1 H), 7.48 (dd, J = 8.0, 1.5 Hz, 1 H), 7.26 (t, J = 8.7 Hz, 1 H), 6.99 (br s, 1 H), 6.87 (t, J = 6.9 Hz, 1 H), 1.51 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 136.3, 132.2, 128.3, 123.8, 120.1, 112.4, 81.0, 28.3. Anal. calc'd for $C_{11}H_{14}BrNO_2$: C, 48.55; H, 5.19; N, 5.15. Found: C, 48.36; H, 5.15; N, 5.06.

***N*-(*t*-Butoxycarbonyl)-1-amino-2-trimethylsilylbenzene (11).** Methyllithium (0.75 mL, 1.2 mmol, 1.6 M in ether) was added dropwise to **9** (0.27 g, 1.0 mmol) in THF/ether (1 mL, 1 mL) at room temperature and stirred for 0.25 h. The mixture was then transferred via cannula into *tert*-butyllithium (1.1 mL, 2.2 mmol, 2.0 M in pentane) in ether (2 mL) at -78°C. The flask and cannula were rinsed with ether (4 mL) and the mixture was allowed to stir for 1 h at -78°C. To the reaction mixture was added trimethylsilyl chloride (0.5 mL, 4 mmol) and the

reaction was allowed to warm to room temperature. The mixture was poured into saturated ammonium chloride solution and the extracted with ether (3x). The combined organic layers were washed with brine and dried over sodium sulfate. The solvent was removed *in vacuo* and the ^{1}H NMR showed that >95% of the contents were the title compound. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 7.3 Hz, 1 H), 7.39 (d, J = 7.3 Hz 1 H), 7.35 (t, J = 7.3 Hz, 1 H), 7.09 (t, J = 7.3 Hz, 1 H), 6.38 (br s, 1 H), 1.49 (s, 9 H), 0.32 (s, 9 H).

***N*-(*t*-Butoxycarbonyl)-2-amino-1-phenylboronic acid (12).** Methyllithium (6.9 mL, 11 mmol, 1.6 M in ether) was added dropwise to **9** (2.7 g, 10 mmol) in THF/ether (15 mL, 5 mL) at room temperature and stirred for 0.5 h. The mixture was then transferred via cannula into *tert*-butyllithium (12.9 mL, 22 mmol, 1.7 M in pentane) in ether (10 mL) at -78°C and allowed to stir for 1 h. The solution was transferred via cannula into trimethylborate (3.637 g, 4.0 mL, 35 mmol) in ether (10 mL) at -78°C and the bath was allowed to warm to room temperature overnight. The mixture was treated with 5% hydrochloric acid (15 mL) for 10 minutes. Sodium chloride was added to the aqueous layer until this phase was close to saturated, then the aqueous layer was extracted with ether (3x). The combined organic layers were extracted with 0.5 M sodium hydroxide solution (20 mL) (6x). The basic extracts were combined and acidified (pH ≈2) with 3 M hydrochloric acid, and then extracted with ether (3x) and dried over sodium sulfate. The solvent was removed *in vacuo* to give 1.78 g (75%) of the title compound. FTIR (KBr) 3335, 2980, 2973, 1729, 1702, 1627, 1583, 1560, 1480, 1451, 1369, 1252, 1157, 759 cm^{-1}. Diethanolamine was added to form the borate ester complex to aid in ^{1}H NMR identification. (300 MHz, $CDCl_3$) δ 9.20 (br s, 1 H), 7.91 (d, J = 8.4 Hz, 1 H), 7.38 (dd, J = 5.7, 2.0 Hz, 1 H), 7.20 (td, J = 6.7, 2.0 Hz, 1 H), 6.93 (td, J = 7.3, 1.5 Hz, 1 H), 5.00 (br s, 1 H), 4.00-3.95 (m, 4 H), 3.30-3.19 (m, 2 H), 2.80-2.70 (m, 2 H), 1.47 (s, 9 H).

6(5*H*)-Phenanthridinone (13).[23] The procedure of Suzuki was followed.[7a] A mixture of methyl 2-bromobenzoate (0.215 g, 1.0 mmol), tetrakis(triphenylphosphine)palladium(0) (0.035 g, 0.03 mmol), and **12** (0.284 g, 1.2 mmol) in toluene (2 mL) with sodium carbonate (1.0 mL of a 2 M solution in deoxygenated water) was

heated at 80-90°C for 38 h. Then the reaction mixture was acidified with hydrochloric acid (3 M) and poured into water. An attempt to extract the aqueous layer with methylene chloride was only partially successful. A white solid that was only slightly soluble in methylene chloride was filtered. The remaining aqueous layer was extracted with methylene chloride (3x). The combined organic layers were washed with saturated sodium bicarbonate and brine followed by drying over sodium sulfate. The solvent was removed *in vacuo* and then purified by flash chromatography [silica gel, methylene chloride/ethyl acetate (9:2)] to give 0.02 g (10.5%) of the title compound which was identical to the 0.100 g (51%) of the white solid recovered earlier. Mp 282-285°C (lit. 285°C). FTIR (KBr) 3448, 3165, 1655, 1609, 1560, 1425, 1384, 1370, 749, 727. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.20 (br s, 1 H), 8.53 (dd, J = 8.5, 1.5 Hz, 1 H), 8.30 (d, J = 8.5 Hz, 1 H), 8.21 (dd, J = 8.0, 1.5 Hz, 1 H), 7.80 (td, J = 8.5, 1.5 Hz, 1 H), 7.60 (td, J = 8.5, 1.5 Hz, 1 H), 7.46 (td, J = 8.5, 1.5 Hz, 1 H), 7.29 (td, J = 8.0, 1.5 Hz, 1 H), 7.20 (dd, J = 8.5, 1.5 Hz, 1 H).

2,5-Dibromo-4-methylbenzoic acid.[12] To nitric acid (45 mL of 70-71%) and water (55 mL) was added 2,5-dibromo-*p*-xylene (13.2 g, 50 mmol) and the mixture was heated to reflux for 6 d (during the reaction sublimation of the starting material occurred and it was reintroduced). The reaction was cooled and the white solid was removed by filtration and the mother liquor was extracted with ether (2x). The extracts were combined with the solid and water (100 mL) and the mixture was sonicated with the slow addition of sodium carbonate (approx. 10 g) over several hours. After all the solids were dissolved, the layers were separated and the aqueous layer was made strongly acidic with concentrated hydrochloric acid. To this slurry were added ether and sodium chloride until the aqueous layer was saturated. The layers were separated and the aqueous layer was extracted with ether (2x). The combined organic fractions were dried over magnesium sulfate. The solvent was removed *in vacuo* and the white solid was purified by recrystallization from hexane (200 mL) and ether (200 mL) to afford 7.02 g (48%) of the title compound as fine white crystals. A subsequent recrystallization afforded 4.67 g (32%) for a total of 80% yield of the title compound. Mp 193 - 195°C. FTIR (KBr) 3200 - 2500, 1684, 1588, 1475, 1426, 1377,

1340, 1300, 1256, 1142, 1057, 931, 902, 872, 783 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (s, 1 H), 7.57 (s, 1 H), 2.41 (s, 3 H).

2,5-Dibromoterephthalic acid (14)[24] prepared by the oxidation of 2,5-dibromo-4-methylbenzoic acid.[12] To potassium permanganate (10.0 g, 63.3 mmol), 2,5-dibromo-4-methylbenzoic acid (7.05 g, 24 mmol) and water (50 mL) was added aqueous saturated sodium bicarbonate solution (50 mL) and the mixture was heated to reflux for 6 d. The reaction mixture was cooled to room temperature and filtered through a pad of celite. The pad was washed with water and saturated sodium bicarbonate solution. To the aqueous solution was carefully added concentrated hydrochloric acid (ether was added to reduce the foaming). Sodium chloride was added to the aqueous solution until saturated and the aqueous layer was extracted with ether (3x). The combined organic fractions were dried over magnesium sulfate. The solvent was removed *in vacuo* to give 7.27 g (94%) of the title compound as a white solid. Mp 308-316°C (lit. 318°C). FTIR (KBr) 3200-2200, 1702, 1472, 1405, 1328, 1286, 1249, 1140, 1064, 915, 780, 660 cm^{-1}.

2,5-Dibromodimethylterephthate (5).[24] To the crude **14** in methanol (150 mL) was carefully added sulfuric acid (5 mL). The mixture was heated to reflux using a Soxhlet extractor equipped with activated 3 Å molecular sieves to remove the water. The sieves were replaced four times over a two day period. Then the mixture was allowed to cool and water was added. The aqueous phase was extracted with methylene chloride (3x). The combined organic fractions were washed with saturated sodium bicarbonate solution and then dried over magnesium sulfate. The solvent was removed *in vacuo* and the crude product was recrystallized from 95% ethanol (150 mL) to give 9.30 g (53% from 2,5-dibromo-*p*-xylene) of the title compound as white crystals. Mp 134-137°C (lit. 137°C). FTIR (KBr) 3085, 2943, 1737, 1420, 1382, 1289, 1245, 1120, 1055, 951, 772 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 2 H), 3.94 (s, 6 H).

Trimer (15). The procedure of Suzuki was followed.[7a] A mixture of **5** (0.106 g, 0.30 mmol), tetrakis(triphenylphosphine)palladium(0) (0.022 g, 0.018 mmol), **12** (0.160 g, 0.68 mmol) in toluene (2.5 mL) with sodium carbonate (1 mL of a 2 M solution in deoxygenated water)

and was heated to reflux (100-110°C) for 38 h. The reaction mixture was poured into a mixture of water and an methylene chloride. The yellow precipitate was collected by filtration and air dried. The compound could not be recrystallized due to its insolubility; therefore the solid was stirred in boiling chloroform and filtered. After drying under vacuum obtained was 27 mg (29%) of the title trimer. Mp > 350°C. FTIR (KBr) 3449, 3033, 2894, 1604, 1596, 1426, 1384, 1351, 748, 728, 639 cm^{-1}. NMR data was not available due to the insolubility of the material. Calc'd for $C_{20}H_{12}N_2O_2$: 312. Found: 312.

Dimer (16). This Suzuki coupling was done using the Gronowitz modification.[7] A mixture of 2'-bromoacetophenone (0.199 g, 0.135 mL, 1 mmol), tetrakis(triphenylphosphine)palladium(0) (0.0347 g, 0.03 mmol) and **12** (0.284 g, 1.2 mmol) in 1,2-dimethoxyethane (2.5 mL) with sodium carbonate (1.2 mL of 2 M in deoxygenated water) and an internal standard, undecane (0.078 g, 0.106 mL, 0.5 mmol) was stirred and heated to reflux (85-90°C) for 7.5 h until the 2'-bromoacetophenone was not detectable by GC. The mixture was cooled to room temperature and sodium sulfate (≈0.5 g) and fuming sulfuric acid (≈0.4 mL) was added until bubbling stopped and a white precipitate was formed, this mixture was allowed to stir for 0.75 h (we later found that fuming sulfuric acid was not necessary, concentrated sulfuric acid would have been sufficient and the drying agent was not necessary). The reaction was then made alkaline with 1 M sodium hydroxide and extracted with ether (3x). The combined organic layers were washed with brine and dried over sodium sulfate. The solvent was removed *in vacuo* and then purified by flash chromatography [silica gel, hexanes/ether (5:1)] to give 0.184 g (95%) of the dimer. Mp 79-81°C. FTIR (KBr) 3060, 2994, 2949, 1612, 1587, 1578, 1373, 752, 722 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, J = 8.3 Hz, 1 H), 8.54 (d, J = 8.0 Hz, 1 H), 8.22 (d, J = 7.5 Hz, 1 H), 8.08 (d, J = 8.1 Hz, 1 H), 7.84 (t, J = 8 Hz, 1 H), 7.69 (t, J = 8 Hz, 2 H), 7.62 (t, J = 8 Hz, 1 H), 3.06 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 143.6, 132.4, 130.3, 129.3, 128.6, 127.2, 126.4, 126.2, 125.7, 123.7, 122.1, 121.9, 23.3. HRMS Calc'd for $C_{14}H_{11}N$: 193.0891. Found: 193.0892.

2,5-Dibromoterephthaloyl dichloride (17). A flask equipped with a reflux condenser and a drying tube was charged with 2,5-dibromoterephthalic acid (7.62 g, 23.5 mmol) and benzene (100 mL). To this mixture was added oxalyl chloride (5.96 g, 4.1 mL, 47 mmol) and one drop of dimethylformamide (catalyst). The reaction mixture was heated to 80°C overnight (bubbling observed), then the reaction was cooled and the solvent was removed *in vacuo*. The crude solid was dissolved in benzene (20 mL) and stirred with calcium hydride for 1 h and then filtered. The benzene was removed *in vacuo* to give 8.49 g (100%) of the title compound. FTIR (KBr) 2979, 1758, 1458, 1412, 1267, 1185, 1074, 836, 801 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 139.6, 137.2, 119.4.

1,4-Bis(1'-oxo-*n*-pentyl)-2,5-dibromobenzene (18). To a slurry of copper(I) cyanide (1.43 g, 16.0 mmol) in THF (25 mL) at -78°C was added *n*-butyllithium (9.3 mL, 14.0 mmol, 1.50 M in hexanes) via syringe pump (0.35 mL per min) and the mixture was then stirred for 3 h. To this solution was added via cannula **17** (1.44 g, 4.0 mmol) in THF (15 mL) and the solution was stirred for 40 min at -78°C. The reaction was quenched at -78°C by the addition of water and the mixture was filtered through a celite pad. The aqueous layer was extracted with ether (3x). The combined organic layers were washed with brine and dried over magnesium sulfate. The solvent was remove *in vacuo* and the product was purified by flash chromatography [silica gel, hexanes/ether (10:1)] to give a white solid which was further purified by recrystallization from 95% ethanol to afford 1.13 g (70%) of the title compound as white needle-like crystals. Mp 86-88°C. FTIR (KBr) 3087, 2950, 2868, 1702, 1468, 1400, 1377, 1354, 1198, 981, 893 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (s, 2 H), 2.87 (t, J = 7.4 Hz, 4 H), 1.67 (p, J = 8.0 Hz, 4 H), 1.4 (sext, J = 8.0 Hz, 4 H), 0.92 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 144.3, 132.9, 117.5, 42.4, 25.9, 22.2, 13.8. Anal. calc'd for $C_{16}H_{20}Br_2O_2$: C, 47.55; H, 4.99; Br, 39.54. Found: C, 47.62; H, 4.94; Br, 39.61. HRMS calc'd for $C_{16}H_{20}{}^{79}Br_2O_2$: 401.9830. Found 401.9829.

Trimer (19). The Gronowitz modification[7] of the Suzuki-coupling was used. To a mixture of **18** (0.202 g, 0.50 mmol), **12** (0.296 g, 1.25 mmol), and

tetrakis(triphenylphosphine)palladium(0) (0.0347 g, 0.03 mmol) in 1,2-dimethoxyethane (2.5 mL) was added sodium carbonate (1.3 mL, 2 M solution in deoxygenated water). The mixture was heated to reflux (80-90°C) for 22 h and then allowed to cool to room temperature. Sulfuric acid (1 mL) was added and the solution was stirred for 0.25 h. The resulting mixture was treated with sodium hydroxide (1 M) until the solution was alkaline and the aqueous phase was extracted with methylene chloride (3x). The combined organic layers were washed with brine solution (used 5 mL of saturated ammonium chloride solution to brake emulsion) followed by drying over sodium sulfate. The solvent was removed *in vacuo* and the product was purified by flash chromatography [silica gel, hexane/ether (3:1)] to afford 0.190 g (97%) of the title trimer. Mp 184-185°C. FTIR (KBr) 3067, 2954, 2932, 2871, 1584, 1490, 1458, 1421, 1384, 1357, 1192, 880, 768, 638 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.49 (s, 2 H), 8.71 (dd, J = 8.5, 2.0 Hz, 2 H), 8.17 (d, J = 8.5 Hz, 2 H), 7.75 (p, J = 8.5 Hz, 4 H), 3.60 (t, J = 8.0 Hz, 2 H), 2.04 (p, J = 8.5 Hz, 4 H), 1.64 (sext, J = 8.5 Hz, 4 H), 1.08 (t, J = 7.4 Hz, 6 H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 162.13, 143.10, 130.17, 129.83, 128.93, 126.77, 125.19, 123.12, 121.56, 119.65, 35.82, 31.06, 23.07, 14.14. HRMS Calc'd for $C_{28}H_{28}N_2$: 392.22525. Found: 392.22549.

2,5-Dibromonitrobenzene.[15] The procedure of Doornbos was modified by using 70.8% nitric acid instead of 97% nitric acid, therefore a large excess of sulfuric acid was used. Sulfuric acid (50 mL) was carefully added to nitric acid (80 mL, 70.8%) and then the mixture was added dropwise to 1,4-dibromobenzene in sulfuric acid (100 mL) at 0°C. The ice bath was allowed to melt and the reaction mixture warmed to room temperature and the suspension was stirred overnight. The mixture was poured into ice and the precipitate was collected and washed with copious amounts of water. The solid was allowed to briefly air dry and then carried on to the next step. Mp 81-83°C (lit. 83.5-84.5°C). ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 2.1 Hz, 1 H), 7.60 (1/2 AB_q, J = 8.5 Hz, 1 H), 7.54 (1/2 AB_qd, J = 8.6, 2.2 Hz, 1 H).

2,5-Dibromoaniline.[15] The procedure by Doornbos was modified as follows. To a solution of tin(II) chloride dihydrate (253 g, 1120 mmol) in concentrated hydrochloric acid (210 mL) at room temperature was added 2,5-dibromonitrobenzene in 95% ethanol (100 mL) as a

slurry. After 15 min an exotherm occurred which rapidly warmed the reaction mixture to reflux. Once the exotherm subsided, the solution was heated to reflux for an additional 0.5 h to ensure complete reduction. The solution was allowed to cool to room temperature and was stirred for several hours. The solid was collected by filtration, briefly air dried, and then suspended in 95% ethanol (235 mL). To this stirring suspension was slowly added 50% sodium hydroxide solution (250 mL) and the mixture was stirred for a few minutes. The mixture was poured into water (1 L) and the solid was collected by filtration and washed with 2 M sodium hydroxide and water to afford, after drying in air, the title compound (61 g) which was used directly in the next step. Mp 53-55°C (lit. 54.5-55°C). FTIR (KBr) 3421, 3321, 1625, 1590, 1474, 1408, 1297, 1143, 1060, 1022, 833, 778 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, J = 8.5 Hz, 1 H), 6.88 (d, J = 2.2 Hz, 1 H), 6.71 (dd, J = 8.4, 2.2 Hz, 1 H), 3.67 (br s, 2 H).

2,5-Dibromoacetanilide.[15] The procedure of Doornbos was followed. Acetic anhydride (86.8 g, 80 mL, 850 mmol) was added dropwise at 0°C to 2,5-dibromoaniline (61.0 g, 243 mmol) in glacial acetic acid (87 mL). After the addition was complete, the mixture was heated to 70° C for 0.25 h and then allowed to cool to room temperature. The excess acetic anhydride was quenched with 100 mL of water and the white solid was collected by filtration and washed with water. After drying, it afforded 65.4 g (80%) of the title compound over three steps. Mp 170-171°C (lit. 172.5-173.5°C). FTIR (KBr) 3282, 1664, 1570, 1519, 1457, 1397, 1280, 1079, 1034, 803, 604 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.57 (br s, 1 H), 7.55 (br s, 1 H), 7.36 (d, J = 8.5 Hz, 1 H), 7.09 (dd, J = 7.6, 2.3 Hz, 1 H), 2.22 (s, 3 H).

2,5-Dibromo-4-nitroacetanilide.[15] *See the main text (eq. 8) for cautions on this procedure.* The procedure by Doornbos was modified as follows. To sulfuric acid (20 mL) was slowly added **20** (8.79 g, 30.0 mmol). A mixture of nitric acid (20 mL, 70.8%) and sulfuric acid (20 mL) was added dropwise over a 2 h period while keeping the temperature between -5 and 5°C. The mixture was allowed to warm to 20°C and stirred for 5 h. The mixture was poured into ice water and the light brown precipitate was collected by filtration. This compound was only allowed to air dry briefly and then was subjected to the following reduction conditions.

1,4-Diamino-2,5-dibromobenzene.[15] The reduction was carried out in a manner analogous to the reduction of 2,5-dibromonitrobenzene using a slurry of 2,5-dibromo-4-nitroacetanilide in 95% ethanol (25 mL) and tin(II) chloride dihydrate (27.0 g, 120 mmol) in concentrated hydrochloric acid (23 mL) over a 20 min period. The reduction was accompanied by the hydrolysis of the acetyl group to afford 4.44 g (56%) of the title compound over two steps. (Crystallized from benzene) Mp 184-187°C (lit. 187-188°C). FTIR (KBr) 3367, 3170, 1499, 1403, 1217, 1053, 877 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.89 (s, 2 H), 3.67 (br s, 4 H).

***N,N'*-Di(*t*-butoxycarbonyl)-1,4-diamino-2,5-dibromobenzene (21).** To a solution of sodium hydride (0.45 g, 15 mmol, 80% dispersion in mineral oil) in THF (50 mL) was added 1,4-diamino-2,5-dibromobenzene (1.29 g, 5.0 mmol). The mixture was heated to reflux for 0.5 h, and then cooled to room temperature. Di-*tert*-butyldicarbonate (2.62 g, 2.8 mL, 12 mmol) and sodium hydride (0.75 g, 25 mmol, 80% dispersion in mineral oil) were added and the mixture was brought back to reflux for 14 h. The reaction was cooled to room temperature and carefully quenched with ethanol then water. The aqueous layer was acidified (pH≈3) with 3 M hydrochloric acid and this mixture was extracted with methylene chloride (3x). The combined organic layers were washed with saturated ammonium chloride solution and saturated sodium bicarbonate solution. After drying over sodium sulfate, the solvent was removed *in vacuo* and the crude material was purified by flash chromatography [silica gel, methylene chloride/hexanes (3:1)] to afford 1.55 g (67%) of the title compound as a crystalline white solid. Mp 199-201°C. FTIR (KBr) 3324, 3083, 2981, 2931, 1701, 1525, 1484, 1449, 1371, 1282, 1243, 1150, 1077, 1047, 1025, 915, 874, 772, 760, 620, 592 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.36 (s, 2 H), 6.86 (br s, 2 H), 1.51 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 131.9, 122.7, 111.6, 81.4, 28.3. Anal. calc'd for $C_{16}H_{22}Br_2N_2O_4$: C, 41.22; H, 4.76; N, 6.01. Found: C, 41.16; H, 4.79; N, 6.01.

2-Bromo-*N*-(*t*-butoxycarbonyl)aniline (9) was prepared via a Curtius rearrangement. The procedure by Pfister was modified as follows.[16] To a mixture of 2-bromobenzoyl chloride (3.45 g, 15.7 mmol) and tetra-*n*-butylammonium bromide (30 mg) in 1,2-

dichloroethane at 0°C was added dropwise a saturated aqueous sodium azide solution (15 mL, approx. 6.4 M). The diphasic mixture was stirred at 0°C for 2.5 h. To this mixture was added ice water and the layers were separated. The organic layer was washed with brine (2x) and dried over magnesium sulfate at 0°C overnight. The drying agent was removed by filtration and the acylazide solution was further dried over calcium hydride at 0°C until bubbling ceased. The calcium hydride was removed by filtration and *tert*-butanol (3.3 g, 4.2 mL, 45 mmol) was added to the acylazide solution and the mixture was heated to 70°C for 2.5 d. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography (silica gel, hexanes/ether, 20:1) to afford 4.11 g (96%) of the title compound as a colorless oil. The analytical data was identical to that described previously.

1,4-Di(acylazidyl)-2,5-dibromobenzene. The procedure by Pfister was followed.[16] Recent reactions have been modified, replacing methylene chloride with 1,2-dichloroethane, since there were reports of explosions when sodium azide was used in methylene chloride.[17] To a mixture of **17** (3.61 g, 10 mmol) and tetra-*n*-butylammonium bromide (80 mg) in methylene chloride (50 mL) at 0°C was added dropwise saturated sodium azide solution (6.25 mL, approx. 6.4 M). The diphasic mixture was stirred at 0°C for 9 h. To this mixture was added cold water and the organic phase was separated. The aqueous layer was extracted with methylene chloride (2x). The combined organic fractions were washed with cold water, brine (2x), and dried over magnesium sulfate (mixture kept at 0°C). The drying agent was removed by filtration and the solution of the diacylazide was taken onto the next step without isolation.

***N,N'*-Di(*t*-butoxycarbonyl)-1,4-diamino-2,5-dibromobenzene (21) prepared using heat to promote the Curtius rearrangement.** The diacylazide was formed as above using **17** (1.082 g, 3.0 mmol) and tetra-*n*-butylammonium bromide (6 mg) in 1,2-dichloroethane (25 mL) and saturated sodium azide solution (6.0 mL, approx. 6.4 M). After drying over magnesium sulfate the drying agent was removed by filtration and the solution was further dried at 0°C using calcium hydride. The calcium hydride was removed by filtration and to the solution of the diacylazide was added *tert*-butanol (3.9 g, 5 mL, 53 mmol) and the solution was heated to 70 -

80°C for 1.5 d. The solvent was removed and the crude solid was purified by flash chromatography (silica gel, methylene chloride) and then recrystallized to afford 0.56 g (56%) of the title compound as white flake-like crystals. The analytical data was identical to that described previously.

***N,N'*-Di(*t*-butoxycarbonyl)-1,4-diamino-2,5-dibromobenzene (21) prepared using *hν* to promote the Curtius rearrangement.** The dry solution of the diacylazide was added to a dry quartz tube containing *t*-butanol (50 mL). The solution was stirred at room temperature and irradiated (TLC UV long wavelength lamp with face removed). Small nitrogen bubbles evolved from the reaction. After 12 h the solution became a suspension with a large amount of yellow solid and the bubbling was very slow. Toluene (50 mL) was added to the reaction to partially dissolve the solid and this suspension was irradiated for an additional 12 h. The solvent was removed *in vacuo* to give 4.15 g (89%) of crude material. The solid was dissolved in methylene chloride/toluene and filtered through a celite pad. The solvent was removed *in vacuo* and the solid was hot filtered with 95% ethanol and toluene and then recrystallized to afford 2.57 g (55%) of the titled compound as off-white fine crystals. A second batch of crystals were also collected 0.163 g (4%). The analytical data was identical to that described previously.

***N,N'*-di(*t*-butoxycarbonyl)-1,4-diamino-2,5-trimethylsilylbenzene (23).** To a slurry of **21** (0.233 g, 0.5 mmol) in ether (2.5 mL) at room temperature was added dropwise methyllithium (0.9 mL, 1.5 mmol, 1.6 M in ether) and the solution was stirred for 10 minutes. The mixture was cooled to -78° C and *tert*-butyllithium (1.8 mL, 3 mmol, 1.7 M in pentane) was added then the temperature was raised to 0° C (ice bath) for 3 h. To this solution was added trimethylsilyl chloride (0.49 g, 0.6 mL, 4.5 mmol). The solution was then allowed to warm to room temperature and stir overnight. The reaction mixture was poured into water and the aqueous layer was extracted with ether (3x). The combined organic fractions were washed with brine and dried over sodium sulfate. The solvent was removed *in vacuo* and the ^{1}H NMR showed that >95% of the contents were the title compound. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (br s, 2 H), 6.19 (br s, 2 H), 1.48 (s, 18 H), 0.31 (s, 18 H).

Diethanolamine [*N*-(t-butoxycarbonyl)-2-amino-1-phenyl]boronate (25). This complex was made using a procedure which was similar to Brown's.[18b] To **12** (0.478 g, 2.0 mmol) was added ether (6 mL), 2-propanol (2 mL), and diethanolamine (0.231 g, 0.211 mL, 2.2 mmol) and stirred at room temperature overnight. A solid formed and it was filtered and washed with cold ether (2 mL) to give 0.479 g (78%) of the title compound. FTIR (KBr) 3257, 3098, 2977, 2892, 1716, 1652, 1605, 1580, 1538, 1440, 1366, 1307, 1278, 1236, 1167, 1104, 874, 852, 748, 720, 524, 494 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.20 (br s, 1 H), 7.91 (d, J= 8.4 Hz, 1 H), 7.38 (dd, J= 5.7, 2.0 Hz, 1 H), 7.20 (td, J= 6.7, 2.0 Hz, 1 H), 6.93 (td, J= 7.3, 1.5 Hz, 1 H), 5.00 (br s, 1 H), 4.00-3.95 (m, 4 H), 3.30-3.19 (m, 2 H), 2.80-2.70 (m, 2 H), 1.47 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 143.3, 133.9, 128.5, 121.9, 118.2, 79.1, 63.3, 51.3, 28.5. HRMS Calc'd for $C_{15}H_{23}{}^{11}BN_2O_4$: 306.1751. Found: 306.1755.

Dimer (16) prepared using 25. The Suzuki coupling was done using the diethanolamine complex under the Gronowitz modification conditions.[7] A mixture of 2'-bromoacetophenone (0.010 g, 0.0675 mL, 0.5 mmol), tetrakis(triphenylphosphine)palladium(0) (0.019 g, 0.015 mmol) and **25** (0.153 g, 0.5 mmol) in 1,2-dimethoxyethane (1.25 mL) with sodium carbonate (0.5 mL of 2 M in deoxygenated water) and an internal standard, undecane (0.078 g, 0.106 mL, 0.5 mmol) was stirred and heated to reflux (85-90 °C) for 43.5 h until the 2'-bromoacetophenone was no longer being consumed. The mixture was cooled to room temperature and sulfuric acid (0.5 mL) was added and stirred for 10 minutes, then 1 M sodium hydroxide was added until alkaline and extracted with ether (3x). The combined organic layers were then washed with saturated brine solution and dried over sodium sulfate. The solvent was removed *in vacuo* and then purified by flash chromatography [silica gel, hexanes/ether (5:1)] to give 0.097 g (25%) of **16**. The analytical data was identical to that described previously.

Dimer (16) prepared using 25 by addition of acetyl chloride followed by aqueous cross-coupling.[7] To a slurry of **25** (0.153 g, 0.50 mmol) and sodium bicarbonate (0.084 g, 1.00 mmol) in dry 1,2-dimethoxyethane (2 mL) at room temperature was added acetyl chloride (0.047 g, 0.043 mL, 0.60 mmol) and the mixture was heated to 80°C for 12 h. To

bis(dibenzylideneacetone)palladium(0) (8.6 mg, 0.015 mmol), and triphenylphosphine (18 mg, 0.068 mmol) was added 1,2-dimethoxyethane (0.5 mL) and the solution was stirred at room temperature for 2 h. To the mixture containing the boron compound was added 2'-bromoacetophenone, (80 mg, 0.054 mL, 0.4 mmol) and saturated aqueous sodium bicarbonate solution (1.8 mL). To the biphasic mixture was added via cannula the yellow catalyst solution. The flask and cannula were rinsed with 1,2-dimethoxyethane (1 mL). The mixture was heated to reflux (80°-85°C) for 25 h. The reaction mixture was allowed to cool to room temperature and 3 M hydrochloric acid (10 mL) was carefully added and the mixture was stirred for 30 min. To this mixture was carefully added saturated sodium bicarbonate solution and the aqueous layer was extracted with ether (4x). The combined organic fractions were washed with brine and dried over sodium sulfate. The solvent was removed *in vacuo* and then purified by flash chromatography [silica gel, hexanes/ether (4:1)] to give 0.077 g (99%) of **16**. The analytical data was identical to that described previously.

Butyl substituted dimer prepared using 25 by addition of acetic anhydride followed by aqueous cross-coupling.[7] To a slurry of **25** (0.306 g, 1.00 mmol) and sodium carbonate (0.055 g, 0.52 mmol) in dry 1,2-dimethoxyethane (2.5 mL) at room temperature was added acetic anhydride (0.112 g, 0.104 mL, 1.10 mmol) and the mixture was stirred for 10 min. The slurry was heated to 80°C for 2 min and allowed to cool to room temperature and stir for 2 h. To the reaction mixture was added 2-bromo-1-(1'-oxo-pentyl)benzene (0.265 g, 0.218 mL, 1.1 mmol), tetrakis(triphenylphosphine)palladium(0) (35 mg, 0.030 mmol), and 2 M sodium carbonate solution (1.1 mL) and the mixture was heated to reflux (80°-85°C) for 21 h. The reaction mixture was allowed to cool to room temperature and 3 M hydrochloric acid was carefully added (until bubbling ceased) and then the mixture was stirred for 2 h. To this mixture was carefully added saturated sodium bicarbonate solution followed by sodium carbonate until the aqueous layer was saturated. The aqueous layer was extracted with methylene chloride (3x). The combined organic fractions were washed with brine and dried over magnesium sulfate. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography [silica gel,

hexanes/ether (10:1)] to give 0.190 g (81%) of the dimer as an oil. FTIR (neat) 3072, 3035, 2957, 2929, 2870, 1612, 1585, 1574, 1527, 1486, 1464, 1446, 1364, 1299, 1236, 1166, 1156, 1103, 1037, 950, 870, 758, 725 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.63 (dd, J = 8.3, 1.5 Hz, 1 H), 8.53 (dd, J = 8.1, 1.5 Hz, 1 H), 8.24 (dd, J = 8.2, 1.5 Hz, 1 H), 8.10 (dd, J = 8.2, 1.1 Hz, 1 H), 7.82 (td, J = 7.0, 1.3 Hz, 1 H), 7.72-7.67 (m, 2 H), 7.60 (td, J = 7.0, 1.3 Hz, 1 H), 3.36 (t, J = 8.0 Hz, 2 H), 1.89 (p, J = 5.0 Hz, 2 H), 1.55 (sext, J = 7.6 Hz, 2 H), 0.99 (t, J = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 143.7, 132.9, 130.2, 129.5, 128.5, 127.2, 126.3, 126.2, 125.2, 123.6, 122.4, 121.9, 36.2, 31.8, 23.1, 14.1. HRMS Calc'd for $C_{17}H_{17}N$: 235.1361. Found: 235.1356.

Pinacol[*N*-(*t*-butoxycarbonyl)-2-amino-1-phenyl]boronate (26). Methyllithium (3.9 mL, 5.5 mmol, 1.4 M in ether) was added dropwise to **9** (1.361 g, 5 mmol) in THF/ether (7.5 mL, 2.5 mL) at room temperature and stirred for 0.5 h. The mixture was then transferred via cannula into *tert*-butyllithium (6.5 mL, 11 mmol, 1.7 M in pentane) in ether (10 mL) at -78°C and allowed to stir for 1 h. To this solution was added trimethylborate (2.60 g, 2.8 mL, 25 mmol) and the reaction mixture was allowed to warm to room temperature for 1 h, then pinacol (3.31 g, 28 mmol) was added and the mixture stirred overnight. The solvent was removed *in vacuo* and the residue was dissolved in methylene chloride and filtered through celite. The solvent was removed *in vacuo* and the crude material was purified by flash chromatography [deactivated silica gel with triethylamine, methylene chloride] to give 1.29 g (81%) of the title compound as a white solid. FTIR (KBr) 3380, 2977, 2934, 1730, 1613, 1584, 1534, 1452, 1355, 1322, 1237, 1156, 1048, 860, 760, 661 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.66 (br s, 1 H), 8.15 (d, J = 8.4 Hz, 1 H), 7.69 (dd, J = 7.4, 1.7 Hz, 1 H), 7.39 (td, J = 8.7, 1.7 Hz, 1 H), 6.96 (td, J = 7.3, 1.0 Hz, 1 H), 1.50 (s, 9 H), 1.34 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 145.3, 136.2, 132.7, 121.5, 117.6, 84.2, 79.7, 28.4, 24.8. HRMS Calc'd for $C_{17}H_{26}{}^{11}BNO_4$: 319.1955. Found: 319.1959.

Dimer (16) prepared using 26. The Suzuki coupling was done using **26** under the Gronowitz modification conditions.[7] A mixture of 2'-bromoacetophenone (0.199 g, 0.135 mL, 1

mmol), tetrakis(triphenylphosphine)palladium(0) (0.0347 g, 0.03 mmol) and **26** (0.383 g, 1.2 mmol) in 1,2-dimethoxyethane (2.5 mL) with sodium carbonate (1.2 mL of 2 M in deoxygenated water) and an internal standard, undecane (0.078 g, 0.106 mL, 0.5 mmol) was stirred and heated to reflux (85-90°C) for 6.25 h until the 2'-bromoacetophenone was not detectable by GC analysis. The mixture was cooled to room temperature and sulfuric acid (0.5 mL) was added and stirred for 10 minutes, then 1 M sodium hydroxide was added until alkaline and extracted with ether (3x). The combined organic layers were then washed with saturated brine solution and dried over sodium sulfate. The solvent was removed *in vacuo* and then purified by flash chromatography [silica gel, hexanes/ether (4:1)] to give 0.184 g (95%) of the dimer. The analytical data was identical to that described previously.

Bispinacol[*N*,*N'*-di(*t*-butoxycarbonyl)-1,4-diamino-2,5-phenyl]diboronate (27). To a slurry of **21** (3.03 g, 6.5 mmol) in ether (10 mL) at room temperature was added dropwise methyllithium (19.5 mL, 19.5 mmol, 1.0 M in ether) and the solution was stirred for 20 minutes. The mixture was cooled to -78° C and *tert*-butyllithium (18.6 mL, 39 mmol, 2.1 M in pentane) was added then the temperature was raised to 0° C (ice bath) for 3 h. To this solution was added methylpinacol borate (7.19 g, 7.7 mL, 45.5 mmol) followed by THF (20 mL). The solution was then allowed to warm to room temperature and stir overnight. Celite (3 g) was added and the mixture was stirred for a few minutes and then the solvent was removed *in vacuo.* Methylene chloride was added and the slurry was stirred for 0.5 h then filtered through a celite pad and washed with methylene chloride. The solvent was removed *in vacuo* and the crude material was chromatographed [Norit A (15 g), Celite 521 (30 g), methylene chloride] followed by a second column [Norit A (25 g), Celite 521 (25 g), methylene chloride]. The solvent was removed *in vacuo* and the crude solid was washed with hexanes to give a white solid (2.57 g) which was recrystallized from hexane/methylene chloride to afford 1.24 g (34%) of the title compound as cubic crystals. A second batch of crystals were collected 0.84 g (23%). FTIR (KBr) 3370, 2980, 2935, 1726, 1560, 1420, 1340, 1271, 1230, 1158, 1096, 1052, 1029, 965, 860, 720, 670 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.48 (br s, 2 H), 8.37 (s, 2 H), 1.50 (s, 18 H), 1.33 (s, 24 H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 139.0, 125.1, 96.0, 84.3, 28.4, 24.9. Anal. calc'd for $C_{28}H_{46}B_2N_2O_8$: C, 60.02; H, 8.27; N, 5.00. Found: C, 60.11; H, 8.33; N, 5.02. HRMS calc'd for $C_{28}H_{46}{}^{10}B_2N_2O_8$: 558.3513. Found: 558.3528.

2-Bromo-1-(1'-oxo-pentyl)benzene. To a slurry of copper(I) cyanide (2.866 g, 32 mmol) in THF (50 mL) at -78°C was added *n*-butyllithium (17.5 mL, 28 mmol, 1.6 M in hexanes) using a syringe pump (0.25 mL per minute). After the addition was complete, the mixture was stirred for 35 min at -78°C. Then 2-bromobenzyl chloride (4.387 g, 20.0 mmol) was added via cannula and the reaction mixture was stirred for 30 min at -78°C, followed by quenching by the addition of water. This mixture was filtered through celite and the aqueous layer was extracted with ether (3x). The combined organic fractions were washed with brine and dried over magnesium sulfate. The solvent was removed *in vacuo* and the crude material was purified by flash chromatography [silica gel, hexanes/ether (25:1)] to give 6.63 g (86%) of a colorless oil. FTIR (neat) 3063, 2959, 2867, 1694, 1652, 1587, 1558, 1506, 1464, 1428, 1360, 1267, 1209, 1054, 1026, 757, 636 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, J = 7.0, 1.1 Hz, 1 H), 7.28-7.23 (m, 3 H), 2.89 (t, J = 7.3 Hz, 2 H), 1.67 (p, J = 5.3 Hz, 2 H), 1.37 (sext, J = 7.5 Hz, 2 H), 0.92 (t, J = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7, 142.1, 133.6, 131.3, 128.2, 127.4, 118.5, 42.5, 26.1, 22.3, 13.9. HRMS Calc'd for $C_{11}H_{13}{}^{79}BrO$: 240.0150. Found: 240.0138.

Trimer (28). The trimer was prepared using modified Suzuki coupling[7] with sodium bicarbonate. To a mixture of 2-bromo-1-(1'-oxo-pentyl)benzene (0.265 g, 1.10 mmol), **27** (0.280 g, 0.50 mmol), sodium bicarbonate (0.252 g, 3.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (64 mg, 0.055 mmol) in 1,2-dimethoxyethane (1.5 mL) was added water (0.75 mL). The mixture was heated to reflux (85-90°C) for 36 h and then allowed to cool to room temperature. To this mixture was slowly added 3 M hydrochloric acid (10 mL) and the solution was stirred overnight. To the mixture was added methylene chloride then sodium carbonate in small portions until the aqueous layer was saturated. The aqueous phase was extracted with methylene chloride (3x). The combined organic fractions were washed with brine

and dried over magnesium sulfate. The solvent was removed *in vacuo* and the crude material was purified by two successive flash columns [deactivated silica gel with triethylamine, methylene chloride] then [silica gel, methylene chloride followed by 5% ethyl acetate in methylene chloride then 10% ethyl acetate in methylene chloride] to afford 0.180 g (92%) of the trimer as a white solid. Mp 186-188°C. FTIR (KBr) 2954, 2923, 2869, 1608, 1589, 1550, 1492, 1458, 1360, 1343, 1312, 1156, 1101, 1037, 879, 768, 670 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.23 (s, 2 H), 8.85 (d, J = 7.9 Hz, 2 H), 8.28 (d, J = 7.5 Hz, 2 H), 7.89 (t, J = 7.0 Hz, 2 H), 7.74 (t, J = 7.0 Hz, 2 H), 3.41 (t, J = 8.0 Hz, 4 H), 1.96 (p, J = 7.6 Hz, 4 H), 1.60 (sext, J = 7.6 Hz, 4 H), 1.03 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 141.4, 132.8, 130.6, 127.7, 126.4, 125.1, 124.5, 123.1, 122.2, 36.4, 31.6, 23.2, 14.1. Anal. calc'd for $C_{28}H_{28}N_2$: C, 85.86; H, 7.19. Found: C, 85.15; H, 7.11.

1,4-Bis(1'-oxo-*n*-tridecane)-2,5-dibromobenzene (29). To a solution of *t*-butyllithium (11.8 mL, 28 mmol, 2.4 M in pentane) in ether (10 mL) at -78°C was added 1-iodododecane (4.44 g,3.7 mL, 15 mmol) dropwise. This solution was stirred for 0.75 h at -78°C. The cold bath was removed and the slurry was transferred via cannula to a slurry of copper(I) cyanide (1.61 g, 18 mmol) in THF (35 mL) at -78°C. The flask and cannula were rinsed with THF (10 mL). The reaction mixture was allowed to stir at -78°C for 4 h then **17** (1.08 g, 3.0 mmol) in THF (20 mL) was cooled to 0°C and was added via cannula to the -78°C solution and stirred for 35 min at -78°C. The reaction was quenched at -78°C by the addition of 9:1 saturated ammonium chloride solution to ammonium hydroxide and the mixture was filtered through a celite pad. The aqueous layer was extracted with ether (3x). The combined organic layers were washed with brine and dried over magnesium sulfate. The solvent was remove *in vacuo* and the product was purified by flash chromatography [silica gel, hexanes/ether (35:1) followed by hexanes/methylene chloride (4:1) and hexanes/methylene chloride (1:1)] to give a white solid which was further purified by recrystallization from hexanes/ether to afford 0.835 g (44%) of the title compound as white cotton-like crystals. A second crop of crystals 0.370 g (20%) were also recovered. Mp 71-74°C. FTIR (KBr) 2917, 2850, 1707, 1467, 1400, 1376, 1341, 1071, 972,

880, 720 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (s, 2 H), 2.86 (t, J = 7.6 Hz, 4 H), 2.66 (p, J = 7.6 Hz, 4 H), 1.24 (m, 36 H), 0.86 (t, J = 6.8 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.7, 144.7, 133.3, 117.9, 43.1, 32.3, 30.01, 30.00, 29.96, 29.8, 29.73, 29.72, 29.5, 24.3, 23.1, 14.5. Anal. calc'd for $C_{32}H_{52}Br_2O_2$: C, 61.15; H, 8.34; Br, 25.42. Found: C, 61.4; H, 8.36; Br, 25.24. HRMS calc'd for $C_{32}H_{52}{}^{79}Br_2O_2$: 626.2334. Found 626.2325.

1-(*tert*-Butyldimethylsiloxy)-6-hydroxyhexane.[19] A procedure by McDougal was modified as follows. To sodium hydride (95%, 1.5 g, 60 mmol) in THF (150 mL) at room temperature was added 1,6-hexanediol (11.8 g, 100 mmol) and the mixture was stirred for 1.5 h. To this slurry *tert*-butyldimethylsilyl chloride (9.0 g, 60 mmol) was added and the mixture was stirred overnight. To this solution water was added and the mixture was extracted with ether (3x). The combined organic fractions were washed with saturated sodium bicarbonate solution, brine, and dried over magnesium sulfate. The solvent was removed *in vacuo* and to the remaining oil, hexanes were added. The solution was cooled to 0°C and the unreacted diol crystallized out. The diol was removed by filtration and the solvent was removed *in vacuo*. To this oil hexanes and a seed crystal of 1,6-hexanediol were added and the mixture was cooled to 0°C. The resulting solid was removed by filtration and the solvent was removed *in vacuo* to give 13.02 g (93%) of the title compound as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 3.62 (t, J = 6.6 Hz, 2 H), 3.59 (t, J = 6.5 Hz, 2 H), 1.60-1.45 (m, 4 H), 1.39-1.27 (m, 5 H), 0.87 (s, 9 H), 0.026 (s, 6 H).

1-(*tert*-Butyldimethylsiloxy)-6-iodohexane. A procedure by Lange[20] was followed. To methylene chloride (250 mL) at room temperature was sequentially added triphenylphosphine (29.7 g, 113 mmol), imidazole (7.7 g, 113 mmol), and iodine (28.7 g, 113 mmol). To this mixture was added via cannula 1-hydroxy-6-(*tert*-butyldimethylsiloxy)hexane (20.16 g, 86.7 mmol) in methylene chloride (40 mL). After the addition was complete, the flask was rinsed with methylene chloride (25 mL) and the mixture was stirred overnight. The solvent was removed *in vacuo*. To this slurry were added sand (3 g), silica gel (10 g), and hexane (50 mL) followed by the removal of the solvent *in vacuo*. The slurry was chromatographed (silica gel, hexanes) to give 23.5 g (86%) of the title compound as a colorless oil. FTIR (neat) 2930, 2857,

1472, 1462, 1388, 1360, 1255, 1206, 1169, 1103, 1006, 836, 775 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 3.58 (t, J = 6.4 Hz, 2 H), 3.17 (t, J = 7.0 Hz, 2 H), 1.81 (p, J = 6.9 Hz, 2 H), 1.57-1.47 (m, 2 H), 1.46-1.27 (m, 4 H), 0.87 (s, 9 H), 0.027 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.9, 33.5, 32.6, 30.3, 26.0, 24.8, 18.3, 6.9, -5.2.

1,4-Bis[7'-(*tert*-butyldimethylsiloxy)-1'-oxo-heptane]-2,5-dibromobenzene. To a solution of *t*-butyllithium (15.4 mL, 37 mmol, 2.4 M in pentane) in ether (15 mL) at -78°C was added via cannula 1-iodo-6-(*t*-butyldimethylsiloxy)hexane (6.29 g, 20 mmol). After the addition was complete, the flask was rinsed with ether (5 mL). This solution was stirred for 1.25 h at -78°C. The cold bath was removed and the slurry was transferred via cannula over a 15 min period to a slurry of copper(I) cyanide (1.97 g, 22 mmol) in THF (25 mL) at -78°C. The flask and cannula were rinsed with THF (10 mL). The reaction mixture was allowed to stir at -78°C for 4 h, then **17** (1.804 g, 5.0 mmol) in THF (15 mL) at 0°C was added via cannula over 40 min and the mixture was stirred for 30 min at -78°C. The reaction was quenched at -78°C by the addition of water and the mixture was filtered through a celite pad. The aqueous layer was extracted with ether (3x). The combined organic layers were washed with brine and dried over magnesium sulfate. The solvent was removed *in vacuo* and the product was purified by Kugelrohr distillation. The lower boiling impurities were removed at 140°C/0.5mm Hg. The product was collected from 160-260°C/0.1-0.05 mm Hg to give 2.76 g (80%) of the title compound as a waxy solid. FTIR (KBr) 2929, 2857, 1709, 1472, 1463, 1388, 1361, 1331, 1256, 1208, 1101, 1074, 1006, 836, 776, 662 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (s, 2 H), 3.58 (t, J = 6.4 Hz, 4 H), 2.87 (t, J = 7.3 Hz, 4 H), 1.69 (p, J = 7 Hz, 4 H), 1.50 (p, J = 7 Hz, 4 H), 1.44-1.30 (m, 8 H), 0.87 (s, 18 H), 0.027 (s, 12 H).

1,4-Bis(7'-hydroxy-1'-oxo-heptane)-2,5-dibromobenzene (30). To 2,5-dibromo-1,4-di[1'-oxo-6'-(*tert*-butyldimethylsiloxy)heptane]benzene (1.36 g, 1.97 mmol) in THF (10 mL) at 0°C was added acetic acid (1.2 g, 1.1 mL, 20 mmol) followed by the dropwise addition of tetrabutylammonium fluoride (10 mL, 10 mmol, 1 M in THF) over 10 min. The reaction mixture was allowed to stir at 0°C for 1 h, then it was slowly warmed to room temperature over a 5

h period as the ice bath melted. The reaction mixture was poured into water and the mixture was extracted with ether (3x). The combined organic fractions were washed with saturated sodium bicarbonate solution (2x) and dried over magnesium sulfate. The solvent was removed *in vacuo* to give 0.86 g (88%) of the crude product as a white solid. The solid was purified by recrystallization from hexanes/ether/methylene chloride to afford 0.54 g (55%) of the title compound as white crystalline needles. FTIR (KBr) 3327, 2930, 2859, 1707, 1461, 1399, 1073, 978, 882 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 2 H), 3.63 (t, J = 6.5 Hz, 4 H), 2.88 (t, J = 7.3 Hz, 4 H), 1.70 (p, J = 6.5 Hz, 4 H), 1.60 (p, J = 6.5 Hz, 4 H), 1.42 (br s, 2 H), 1.41-1.30 (m, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 144.3, 132.9, 117.6, 62.8, 42.6, 32.5, 28.8, 25.5, 23.7. HRMS calc'd for $C_{20}H_{28}{}^{79}Br_2O_4$ = 490.0354. Found 490.0356.

1-Bromo-4-trimethylsilylbenzene. To 1,4-dibromobenzene (11.80 g, 50 mmol) in THF (100 mL) at -78°C was added *n*-butyllithium (31.3 mL, 50 mmol, 1.6 M in hexane) dropwise over 15 min. The slurry was stirred for 1.5 h at -78°C followed by the addition of trimethylsilyl chloride (8.15 g, 75 mmol). The reaction was allowed to warm to room temperature over 1 h. To the solution was added water and the layers were separated. The aqueous phase was extracted with ether (2x). The combined organic fractions were washed with saturated sodium bicarbonate solution, brine, and dried over magnesium sulfate. The solvent was removed *in vacuo* to afford 11.38 g (99%) of the titled compound. FTIR (neat) 2956, 1574, 1479, 1376, 1250, 1106, 1067, 1012, 840, 807, 755, 719, 626 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 7.9 Hz, 2 H), 7.35 (d, J = 7.9 Hz, 2 H), 0.24 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 135.0, 131.0, 123.7, –1.1. HRMS calc'd for $C_9H_{13}Si^{79}Br$: 227.9970. Found: 227.9966.

1-(1'-Octynyl)-4-trimethylsilylbenzene. To 1-octyne (3.1 g, 3.9 mL, 28 mmol) in THF (25 mL) at -78°C was added dropwise *n*-butyllithium (16.9 mL, 27 mmol, 1.6 M in hexanes) and the reaction mixture was stirred for 1 h. To flame dried zinc chloride (5.45 g, 40 mmol) in THF (15 mL) at 0°C was transferred via cannula the solution of the lithium acetylide. The mixture was allowed to warm to room temperature where it stirred for 1.5 h. To this solution were added via cannula tetrakis(triphenylphosphine)palladium(0) (0.69 g, 0.6 mmol) and 1-bromo-4-

trimethylsilylbenzene (4.58 g, 20 mmol). The flask and cannula were rinsed with THF (10 mL). The reaction mixture was heated to reflux for 20 h until the disappearance of starting material by capillary GC analysis. The reaction mixture was cooled to room temperature and 3 g of celite were added and the resulting slurry was filtered through a pad of celite. The celite pad was rinsed with hexane. The solvent was removed *in vacuo*. The crude product was purified by flash chromatography (silica gel, hexanes) to afford 5.15 g (100%) of the title compound as a colorless oil. FTIR (neat) 3065, 3018, 2956, 2930, 2858, 2227, 1596, 1500, 1466, 1458, 1390, 1378, 1330, 1305, 1249, 1109, 840, 820, 757, 716, 692 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 8.2 Hz, 2 H), 7.35 (d, J = 8.2 Hz, 2 H), 2.39 (t, J = 7.1 Hz, 2 H), 1.59 (p, J = 7.2 Hz, 2 H), 1.43 (p, J = 6.7 Hz, 2 H), 1.32 - 1.28 (m, 4 H), 0.89 (t, J = 6.9 Hz, 3 H), 0.23 (s, 9 H).

1-Octyl-4-trimethylsilylbenzene. To 1-(1'-octynyl)-4-trimethylsilylbenzene (5.15 g, 20 mmol) and 10% palladium on carbon (0.3 g) was added ethanol (100 mL) and the mixture was placed on a Parr Shaker starting with 50 psi of hydrogen. The reduction was allowed to run overnight. The mixture was filtered and the solvent was removed *in vacuo* to give 5.03 g (97 %) of the title compound as a colorless oil. FTIR (neat) 3066, 3010, 2956, 2926, 2855, 1602, 1466, 1396, 1378, 1248, 1109, 838, 804, 755, 722, 692, 659, 642 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 7.9 Hz, 2 H), 7.16 (d, J = 7.7 Hz, 2 H), 2.57 (t, J = 7.8 Hz, 2 H), 1.60 (p, J = 7.7 Hz, 2 H), 1.30 - 1.23 (m, 10 H), 0.86 (t, J = 7.7 Hz, 3 H), 0.24 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 137.1, 133.4, 128.0, 36.1, 32.0, 31.6, 29.61, 29.56, 29.4, 22.8, 14.2, −1.0. HRMS calc'd for $C_{17}H_{30}Si$: 262.2117. Found: 262.2105.

1-Bromo-4-octylbenzene. To 1-octyl-4-trimethylsilylbenzene (4.82 g, 18.4 mmol) in methylene chloride (40 mL) at -78°C was added dropwise bromine (2.94 g, 0.95 mL, 18.4 mmol). After the addition was complete the reaction stirred for 8 min and then the solution became a frozen slurry. The -78°C bath was removed and the reaction was allowed to warm until the reaction became a homogeneous solution. The reaction was quenched with an aqueous sodium thiosulfate solution. After the mixture warmed to room temperature the layers were separated and the aqueous layer was extracted with methylene chloride (2x). The combined organic fractions were washed

with 3 M hydrochloric acid, brine, and dried over magnesium sulfate. The solvent was removed *in vacuo* and the crude product was purified by Kugelrhor distillation (110°C at 0.25 mm Hg). This product was filtered through a silica gel plug (hexane) to afford 4.79 g (97%) of the title compound as a light yellow oil. FTIR (neat) 2926, 2855, 1488, 1466, 1403, 1378, 1073, 1012, 799, 722 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4, Hz, 2 H), 7.03 (d, J = 8.5, Hz, 2 H), 2.53 (t, J = 7.9 Hz, 2 H), 1.56 (p, J = 7.6 Hz, 2 H), 1.30 - 1.20 (m, 10 H), 0.86 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 131.3, 130.2, 119.3, 35.5, 32.0, 31.4, 29.6, 29.4, 29.3, 22.8, 14.2. HRMS calc'd for $C_{14}H_{21}{}^{79}Br$: 268.0827. Found: 268.0830.

Ketone 31. To a solution of *t*-butyllithium (19.2 mL, 40 mmol, 2.08 M in pentane) in ether (15 mL) at -78°C was added dropwise via cannula 1-bromo-4-octylbenzene (5.92 g, 22 mmol). The flask was rinsed with ether (15 mL). The reaction mixture stirred for 1 h at -78°C. The slurry was then transferred via cannula to flame dried zinc chloride (5.45 g, 22 mmol) in THF (10 mL) at 0°C. The flask was rinsed with THF (10 mL) and the mixture was allowed to warm to room temperature over 1 h. The solution was cooled to 0°C and **17** (1.80 g, 5 mmol) was added. To a test tube containing bis(dibenzylideneacetone)palladium(0) (0.173 g, 0.3 mmol), and triphenylphosphine (0.59 g, 2.25 mmol) was added THF (2 mL) and the brown slurry was stirred at room temperature until the color changed to yellow. This solution of the palladium(0) catalyst was transferred via cannula to the reaction mixture and the mixture was stirred at 0°C for 22 h. The reaction was quenched at 0°C with water followed by the addition of 3 M hydrochloric acid. The mixture was separated and the aqueous layer was extracted with ether (2x). The combined organic fractions were washed with saturated sodium bicarbonate solution, brine, and dried over magnesium sulfate. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography [silica gel, hexanes followed by hexanes/methylene chloride, 8:1 (450 mL) and 3:1 (600 mL)] to give a waxy white solid. The compound was further purified by recrystallization from hexanes/ether to afford 1.51 g (45%) of the title compound as white crystals. Subsequent recrystallization from the mother liquor afforded a second crop of crystals 0.275 g (8%). FTIR (KBr) 2956, 2924, 2853, 1668, 1604, 1467, 1416, 1345, 1250, 1184, 1152, 1060,

934, 882, 852, 756, 668 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 4 H), 7.56 (s, 2 H), 7.30 (d, J = 8.4 Hz, 4 H), 2.68 (t, J = 7.9 Hz, 4 H), 1.63 (p, J = 7.9 Hz, 4 H), 1.40 - 1.20 (m, 20 H), 0.86 (t, J = 7.0 Hz, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 150.9, 143.8, 133.35, 133.32, 130.9, 129.4, 118.8, 36.6, 32.3, 31.4, 29.8, 29.7, 29.6, 23.1, 14.5. Anal. calc'd for $C_{36}H_{44}Br_2O_2$: C, 64.68; H, 6.63; Br, 23.90. Found: C, 64.75; H, 6.68; Br, 24.00.

Polymer 32 prepared by aqueous cross-coupling. The polymer was prepared using a modified Suzuki-coupling[7] with sodium bicarbonate. To bis(dibenzylideneacetone)palladium(0) (0.029 g, 0.05 mmol), and triphenylphosphine (0.059 g, 0.225 mmol) was added 1,2-dimethoxyethane (1.5 mL) and the mixture was stirred at room temperature for 3 h. To this yellow solution was added **18** (0.202 g, 0.50 mmol), **27** (0.308 g, 0.55 mmol), sodium bicarbonate (0.30 g, 3.6 mmol), and a saturated sodium bicarbonate solution (0.75 mL). The mixture was heated to reflux (85-90°C) for 3.5 d and then allowed to cool to room temperature. To this mixture was added water and the aqueous layer was extracted with methylene chloride (3x). The combined organic fractions were washed with brine and dried over sodium sulfate. The solvent was removed *in vacuo* and the crude material was dissolved in a minimal amount of 2:1 ether/THF and then fractionally precipitated by pouring into methanol (100 mL). The solid was collected by filtration to give 0.174 g (63%) of the uncyclized polymer **32**. FTIR (film) 3430, 2959, 2872, 1728, 1694, 1682, 1674, 1532, 1456, 1393, 1368, 1231, 1154, 1052, 1025, 895, 767, 694 cm^{-1}. ^1H NMR (300 MHz, C_6D_6) δ 8.5 - 6.8 (br m), 2.8 - 2.3 (br m), 1.8 - 0.6 (br m). ^{13}C NMR (125 MHz, C_6D_6) δ 207.0 - 198.5, 158.4 - 154.1, 153.1 - 151.9, 148.0 - 139.4, 137.5 - 115.0, 91.9 - 90.2, 85.8 - 82.5, 82.0 - 80.4, 43.7 - 38.3, 37.0 - 24.8, 24.7 - 22.5, 15.0 - 12.7. M_n = 9,850, M_w/M_n = 1.85. λ (CH_2Cl_2) = 250, 306 (sh) nm. λ (film) = 196, 248 (s), 308 nm. ^{13}C NMR (125 MHz, C_6D_6) δ 207.0 - 198.5, 158.4 - 154.1, 153.1 - 151.9, 148.0 - 139.4, 137.5 - 115.0, 91.9 - 90.2, 85.8 - 82.5, 82.0 - 80.4, 43.7 - 38.3, 37.0 - 24.8, 24.7 - 22.5, 15.0 - 12.7. Anal. calc'd for $(C_{32}H_{42}N_2O_6)_n$: C, 69.79; H, 7.69; N, 5.07. Found: C, 70.55; H, 7.25; Br, <0.5, N, 5.13.

Polymer 33 prepared by aqueous cross-coupling. The polymer was prepared using a modified Suzuki-coupling[7] with sodium bicarbonate. To bis(dibenzylideneacetone)palladium(0) (0.029 g, 0.05 mmol), and triphenylphosphine (0.059 g, 0.225 mmol) was added 1,2-dimethoxyethane (1.0 mL) and the solution was stirred at room temperature for 1.5 h. To this yellow suspension was added **29** (0.314 g, 0.5 mmol), **27** (0.280 g, 0.5 mmol), sodium bicarbonate (0.28 g, 3.3 mmol), saturated aqueous sodium bicarbonate solution (1.0 mL), and 1,2-dimethoxyethane (0.75 mL). The mixture was heated to reflux (85-90°C) for 1 d, then **27** (0.014 g, 0.025 mmol) was added and the mixture was heated for and additional 2.5 d. Then the reaction was allowed to cool to room temperature. To this mixture was added water and the aqueous layer was extracted with methylene chloride (3x). The combined organic fractions were washed with brine and dried over sodium sulfate. The solvent was removed *in vacuo* and the crude material was dissolved in a minimal amount of ether and then fractionally precipitated by pouring into methanol (100 mL). The solution was centrifuged, the methanol was decanted, and the remaining solid was dried *in vacuo* to give 0.374 g (97%) of the uncyclized polymer **33**. FTIR (film) 3431, 2925, 2854, 1733, 1687, 1531, 1466, 1368, 1342, 1228, 1155, 1052, 894, 767 cm^{-1}. ^1H NMR (300 MHz, C_6D_6) δ 9.0 - 6.8 (br m), 2.9 - 1.1 (br m), 1.05 - 0.85 (br s). ^{13}C NMR (125 MHz, C_6D_6) δ 157.0 - 155.2, 153.6 - 152.4, 146.4 - 140.6, 137.6 - 118.5, 90.2 - 89.4, 84.0 - 82.1, 81.2 - 79.4, 43.0 - 41.5, 41.4 - 40.0, 37.0 - 34.8, 32.4, 30.9 - 29.1, 28.3, 25.2 - 23.3, 14.4. M_n = 28,400, M_w/M_n = 3.70. λ (CH_2Cl_2) = 250, 388 nm. λ (film) = 196, 250, 398 nm. Anal. calc'd for $(C_{48}H_{74}N_2O_6)_n$: C, 74.38; H, 9.62; N, 3.61. Found: C, 74.99; H, 9.40; Br, <0.5; N, 3.55.

Polymer 34 prepared by aqueous cross-coupling. The polymer was prepared using a modified Suzuki-coupling[7] with sodium bicarbonate. To bis(dibenzylideneacetone)palladium(0) (0.029 g, 0.05 mmol), and triphenylphosphine (0.059 g, 0.225 mmol) was added 1,2-dimethoxyethane (1.0 mL) and the mixture was stirred at room temperature for 2.5 h. To this yellow suspension was added **30** (0.246 g, 0.5 mmol), **27** (0.280 g, 0.5 mmol), sodium bicarbonate (0.378 g, 4.5 mmol), and a saturate sodium bicarbonate

solution (1.0 mL, 1.2 mmol) was added 1,2-dimethoxyethane (0.75 mL). The mixture was heated to reflux (85 - 90°C) and after 1 d 1,2-dimethoxyethane (0.5 mL) was added to the mixture due to an increase in viscosity, and the reaction mixture was further heated for and additional 2.5 d. Then the reaction was allowed to cool to room temperature. To this mixture was added water and the solid material was removed by filtration. No organic solvent could be found to dissolve the solid which was 0.267 g (82%).

Polymer 35 prepared by aqueous cross-coupling. The polymer was prepared using a modified Suzuki-coupling[7] with sodium bicarbonate. To bis(dibenzylideneacetone)palladium(0) (0.029 g, 0.05 mmol), and triphenylphosphine (0.059 g, 0.225 mmol) was added 1,2-dimethoxyethane (1.0 mL) and the mixture was stirred at room temperature for 1.5 h. To this yellow suspension were added **31** (0.334 g, 0.5 mmol), **27** (0.280 g, 0.5 mmol), sodium bicarbonate (0.28 g, 3.3 mmol) and saturated sodium bicarbonate solution (1.0 mL, 1.2 mmol). The mixture was heated to reflux (85-90°C) and after 1 d, **27** (0.014 g, 0.025 mmol) was added and the mixture was heated for and additional 2.5 d. During the 2.5 d interval, 1,2-dimethoxyethane (1.5 mL) was added due to a lose of some solvent and to keep the polymer in solution. Then the reaction was allowed to cool to room temperature. To this mixture was added water and the aqueous layer was extracted with methylene chloride (3x). The combined organic fractions were washed with brine and dried over sodium sulfate. The solvent was removed *in vacuo* and the crude material was dissolved in a minimal amount of ether/THF (2:1) and then fractionally precipitated by pouring into methanol (100 mL). The mixture was allowed to stand at room temperature for 3 d to evaporate most of the ether/THF. The solution was centrifuged, the methanol was decanted, and the remaining solid was dried *in vacuo* to give 0.328 g (80%) of the uncyclized polymer **35**. FTIR (film) 3298, 2924, 2854, 1728, 1666, 1604, 1534, 1456, 1366, 1228, 1224, 1156, 1052, 954, 844, 772 cm^{-1}. ^1H NMR (300 MHz, C_6D_6) δ 8.20 - 7.62 (br m), 7.20 - 6.80 (br m), 2.78 - 2.20 (br m), 1.70 - 1.40 (m), 1.40 - 1.10 (m), 1.0 - 0.80 (m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.5 – 195.0, 154.2 – 152.0, 151.0 – 149.0, 143.8 – 140.0, 139.0 – 127.8, 126.0 – 121.8, 81.5 – 80.0, 37.0 – 36.0, 32.4 – 32.0, 31.8 – 31.0, 30.0

– 29.2, 29.0 – 28.0, 23.2 – 22.8, 14.6 – 14.4. M_n = 18,500 M_w/M_n = 2.75. λ (CH_2Cl_2) = 254 nm. λ (film) = 254 nm. Anal. calc'd for $(C_{52}H_{66}N_2O_6)_n$: C, 76.62; H, 8.16; N, 3.44. Found: C, 76.01; H, 7.85; Br, < 0.5; N, 3.43.

Cyclization of 32 to 36. To the uncyclized polymer **32** (0.093 g, 0.169 mmol) in methylene chloride (10 mL) at room temperature was added trifluoroacetic acid (4 mL). The brown solution was heated to reflux overnight. The solution was cooled to room temperature and the solvent was removed *in vacuo*. To this brown solid was added 3 M sodium hydroxide (30 mL) and THF (30 mL) and the mixture was stirred at room temperature for 1 d. The solid was collected by filtration then washed with water, methylene chloride and ether. To this solid in a screw cap tube was added triethylamine and the mixture was heated to 160°C for 14 h. The mixture was allowed to cool to 50 - 60°C and the solid was collected by filtration then washed with water, ether, and methylene chloride. The solid was dried *in vacuo* to give 0.048 g (90%) of the cyclized material. FTIR (KBr) 2956, 2929, 2870, 1578, 1498, 1459, 1420, 1400, 1364, 1113, 876, 624 cm^{-1}. λ (CH_2Cl_2/TFA) = 374, 396, 426 (sh), 514, 520 (ed). Anal. calc'd for $(C_{22}H_{22}N_2)_n$: C, 84.04; H, 7.05; N, 8.91. Found: C, 79.13; H, 6.77; Br, <0.5; N, 8.56.

Cyclization of 33 to 37. To the uncyclized polymer **33** (0.166 g, 0.214 mmol) in methylene chloride (15 mL) at room temperature was added trifluoroacetic acid (5 mL). The brown solution was heated to reflux overnight. The solution was cooled to room temperature and the solvent was removed *in vacuo*. To this brown solid was added 3 M sodium hydroxide (40 mL) and THF (40 mL) and the mixture was stirred at room temperature for 2 d. The solid was collected by filtration then washed with water and ether. To this solid in a screw cap tube was added triethylamine and the mixture was heated to 160°C for 14 h. The mixture was allowed to cool to 50 - 60°C and the solid was collected by filtration then washed with water, ether, and methylene chloride. The solid was dried *in vacuo* to give 0.112 g (97%) of the cyclized material. FTIR (KBr) 2921, 2851, 1578, 1499, 1466, 1365, 1117, 879, 721, 627 cm^{-1}. λ (CH_2Cl_2/TFA) = 376, 400, 428, 478, 516, 530 (ed) nm. λ_{max} (solid) = 463-490 nm. Anal. calc'd for $(C_{38}H_{54}N_2)_n$: C, 84.70; H, 10.10; N, 5.20. Found: C, 81.45; H, 9.64; Br, <0.5; N, 5.22.

Cyclization of dodecyl substituted polymer 33 to form films of 37. The uncyclized polymer (**33**) was formed as a film by removal of THF *in vacuo* on a rotary evaporator (films can also be formed by casting the uncyclized polymer on glass plates and allowing slow evaporation of THF). This film was then treated with 3 M hydrogen chloride in dry ethyl acetate and the film turned a reddish brown. This mixture was allowed to sit overnight and then a piece of the film was removed and placed in triethylamine. Over 15 - 30 min, the film became yellow. After 3 h, the film was removed and washed with water and ether. The FTIR spectrum showed (absorbances from 2750 - 2499 cm^{-1}) that there was some hydrochloride salt on the polymer. Adding this polymer to a mixture of triethylamine and 3 M sodium hydroxide for 1 d at room temperature removed the remaining acid. The film was washed with water and ether to give a free standing flexible film. FTIR (film) 2921, 2852, 1582, 1497, 1467, 1399, 1365, 1316, 1149, 881, 721, 626 cm^{-1}.

Cyclization of polymer 35 to form films of 38. These films were prepared analogously to the above procedure.

Cyclization of 35 to 38. To the uncyclized polymer **35** (62.5 mg, 0.08 mmol) in methylene chloride (3 mL) at room temperature was added trifluoroacetic acid (3 mL). The brown solution was heated to reflux for 12 h. The solution was cooled to room temperature and the solvent was removed *in vacuo*. To this brown solid was added saturated sodium bicarbonate (10 mL), triethylamine (1 mL) and THF (10 mL) and the mixture was stirred at room temperature for 12 h. The solid was collected by filtration then washed with water, ether and ethyl acetate. To this solid in a sealed tube was added triethylamine and the mixture was heated to 140 - 150°C for 1.5 d. The mixture was allowed to cool to room temperature then the solid was collected by filtration then washed with water, ether, and methylene chloride. The solid was dried *in vacuo* to give 46 mg (99%) of the cyclized material **38**. FTIR (KBr) 3025, 2954, 2923, 2852, 1610, 1572, 1560, 1492, 1499, 1453, 1408, 1359, 1321, 1265, 1181, 1118, 956, 888, 798 cm^{-1}. λ_{max} (CH_2Cl_2/TFA) = 356, 376, 402, 458, 506, 549, 580 (ed) nm. λ_{max} (suspended film in ethyl

acetate) = 482 nm. Anal. calc'd for $(C_{42}H_{46}N_2)_n$: C, 87.15; H, 8.01; N, 4.84. Found: C, 82.68; H, 7.80; Br, <0.5; N, 4.99.

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(1) **Table I.** Optical Absorption Data

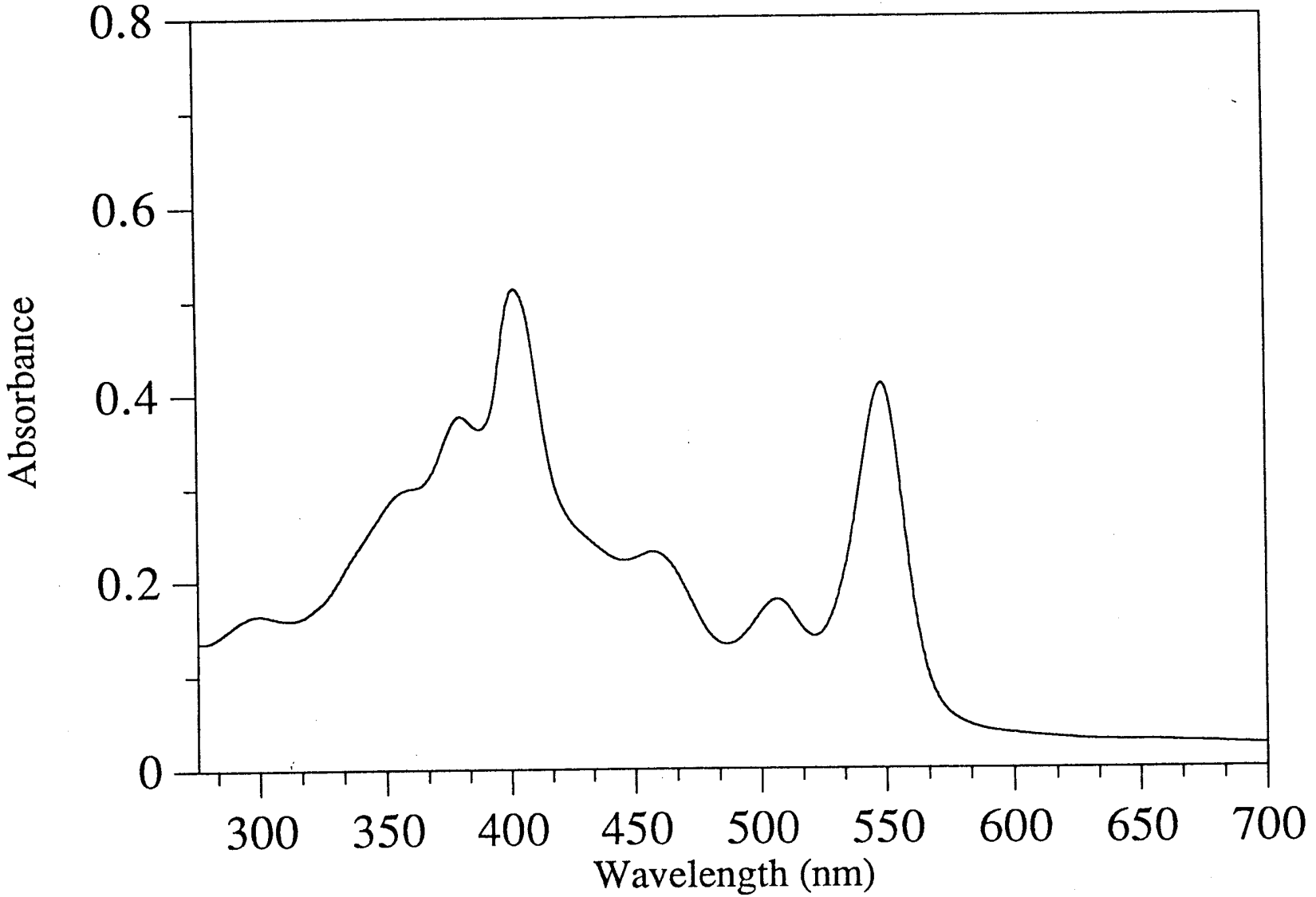
(2) **Figure 3.** UV-Vis spectrum of **38** in a solution of CH_2Cl_2/TFA, 2:3.

Table I. Optical Absorption Data

Compound	λ in solution (nm)[a]	λ of solid (nm)[a]
32	CH_2Cl_2: 250, 306 (sh)	248, 308[b]
33	CH_2Cl_2: 250, 388	250, 398[b]
35	CH_2Cl_2: 254	254
36	CH_2Cl_2/TFA: 374, 396, 426 (sh), 514, 520 (ed)[c]	---
37	CH_2Cl_2/TFA: 376, 400, 428, 478, 516, 530 (ed)[c]	463-490[d]
38	CH_2Cl_2/TFA: 356, 376, 402, 458, 506, 549, 580 (ed)[c]	482
19	CH_2Cl_2: 300	---
28	CH_2Cl_2: 294	---
p-sexiphenylene	$CHCl_3$: 318 (ref 21)	---
PPP (calcd infinite M_n)	344 (ref 21)	---

[a]λ_{max} is underlined, (sh) is shoulder, (ed) is tailing edge at ~10% of λ_{max} intensity. [b]Also a strong carbonyl absorption at 196 nm. [c]Spectrum recorded on the acid solublized, therefore, multiprotonated system. [d]These λ_{max} values were recorded on a series of four different polymer samples of **37** in order to insure their reproducibility.[22]

Fig 3


0.8
0.6
0.4
0.2
0
Absorbance
300
350
400
450
500
550
600
650
700
Wavelength (nm)